

Table 15.87. The symbols of functional groups of alkyl aldehydes.

Functional Group	Group Symbol
CH ₂ (formaldehyde) group	$C-H (CH_2)$ (i)
CH (aldehyde) group	CH (i)
C=O	$C=O$ (i)
C-C(O)H	$C-C(O)H$
CH ₃ group	$C-H (CH_3)$
CH ₂ (alkyl) group	$C-H (CH_2)$ (ii)
CH (alkyl)	$C-H$ (ii)
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 5.88. The geometrical bond parameters of alkyl aldehydes and experimental values [1].

Parameter	$C-H$ (i) (CH_2) Group	$C-H$ (i) Group	$C=O$ Group	$C-C(O)H$ Group	$C-H$ (CH ₃) Group	$C-H$ (CH ₂) (ii) Group	$C-H$ (iii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
σ (e _s)	1.64010	1.67465	1.29907	2.04740	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
c' (e _s)	1.04566	1.05661	1.13977	1.43087	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c^*$ (Å)	1.10668	1.11827	1.20628	1.51437	1.09974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $2c^*$ (Å)	1.116 (formaldehyde)	1.128 (acetaldehyde)	1.208 (formaldehyde) 1.210 (acetaldehyde)	1.515 (acetaldehyde)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$4.c$ (e _s)	1.26354	1.29924	0.63331	1.66439	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
σ	0.63756	0.65095	0.87737	0.69887	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.89. The MO to HO intercept geometrical bond parameters of alkyl aldehydes. R, R', R'' are H or alkyl groups. E_T is $E_T(\text{atom} - \text{atom}, \text{exp})$, ΔO .

Band	Atom	E_T (eV) Bond 1	F_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy (eV)	r_{final} (a ₀)	r_{initial} (a ₀)	E_{kinetic} (eV) Final	$\mathcal{E}(\text{C}_{2v}^{\text{opt}})$ (°) Final	θ_i (°)	θ_s (°)	d_i (a ₀)	d_s (a ₀)
$H^+(O) - H \text{ (CH}_2 \text{)} (i)$	C	-1.34046	0	0	0	-152.96515	0.91771	0.84115	-16.17521	-15.98435	104.28	40.18	1.25314	0.20748
$-C_1^+ H_2 C_2 (O) - H \text{ (CH)} (i)$	C ₁	-1.34046	-0.92918	0	0	-153.89434	0.91771	0.79546	-17.10440	-16.91353	64.95	35.69	1.39945	0.33684
$H_2 C_2 = O$	O	-1.34046	0	0	0	1.00000	0.84115	0.84115	-16.17521	137.27	42.73	66.31	0.51193	0.61784
$-C_1 H_2 C_2 (H) = O$	O	-1.34046	0	0	0	1.00000	0.84115	0.84115	-16.17521	137.27	42.73	66.31	0.51193	0.61784
$RH_2 C_2 - C_1 (H) (O)$	C ₁	-1.34046	-0.92918	0	0	-153.89434	0.91771	0.79546	-17.10440	-16.91353	135.34	44.44	0.57401	0.65675
$H_2 C_2 - C_1 (H) (O)$	C ₁	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.54593	-15.56007	72.37	34.17	1.69388	0.56301
$-C_2 H_2 - C_1 (H) (O)$	C ₁	-0.92918	-0.92918	0	0	-153.17405	0.91771	0.81549	-16.68411	-16.49255	65.99	14.01	1.76710	0.33113
$C - H \text{ (CH}_2 \text{)}$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.54593	-15.56007	77.49	102.51	1.23564	0.18708
$C - H \text{ (CH}_2 \text{)} (ii)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49255	64.47	111.53	1.53486	0.29923
$C - H \text{ (CH)} (ii)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42344	61.10	118.90	1.42988	0.37326
$H_2 C_2^+ H_2 C_2^-$	C ₁	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.54593	-15.56007	63.82	30.08	1.83979	0.38106
$(C - C) (a)$	C ₁	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.54593	-15.56007	63.82	30.08	1.83979	0.38106
$H_2 C_2^+ H_2 C_2^-$	C ₁	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49255	56.41	123.59	1.90890	0.45117
$R - H_2 C_2 (H_2 C_2 - R) HCH_2 -$ (C - C) (b)	C ₁	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42344	48.30	131.70	1.97162	0.51388
$R - H_2 C_2 (R' - H_2 C_2) C_1 (R' - H_2 C_2) CH_2 -$ (C - C) (c)	C ₁	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75899	-17.92866	-17.73779	48.21	131.79	1.95724	0.50570
$isoC_1 C_1 (H_2 C_2 - R') HCH_2 -$ (C - C) (d)	C ₁	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42344	44.30	131.70	1.97162	0.51388
$isoC_1 C_1 (R' - H_2 C_2) C_1 (R' - H_2 C_2) CH_2 -$ (C - C) (e)	C ₁	-0.72457	-0.72457	-0.72457	-0.72457	-154.51999	0.91771	0.76365	-17.92866	-17.73779	50.04	129.96	1.94462	0.49298
$isoC_1 C_1 (H_2 C_2 - R') HCH_2 -$ (C - C) (f)	C ₁	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.31783	52.78	127.22	1.92443	0.47279
$isoC_1 (R' - H_2 C_2) C_1 (R' - H_2 C_2) CH_2 -$ (C - C) (g)	C ₁	-0.72457	-0.72457	-0.72457	-0.72457	-154.51999	0.91771	0.76365	-17.92866	-17.73779	50.04	129.96	1.94462	0.49298

Table 15.90. The energy parameters (eV) of functional groups of alkyl aldehydes.

Parameters	$\text{C}=\text{O}$ Group	$\text{C}-\text{O}$ Group	$\text{C}-\text{C}(\text{O})\text{H}$ Group	CH_2 Group	CH_3 Group	CH_2 Group	CH_3 Group	$\text{C}-\text{C}(\text{a})$ Group	$\text{C}-\text{C}(\text{b})$ Group	$\text{C}-\text{C}(\text{c})$ Group	$\text{C}-\text{C}(\text{d})$ Group	$\text{C}-\text{C}(\text{e})$ Group	$\text{C}-\text{C}(\text{f})$ Group
η_1	2	1	2	1	3	2	1	1	1	1	1	1	1
η_2	1	0	0	0	2	1	0	0	0	0	0	0	0
η_3	0	0	0	0	0	0	0	0	0	0	0	0	0
ζ_1	0.75	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
ζ_2	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_3	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_4	0.91771	0.91771	0.85295	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
ζ_5	1	0	2	0	0	1	1	0	0	0	1	1	0
ζ_6	1	1	4	2	1	1	1	2	2	2	2	2	2
ζ_7	2	1	0	0	3	2	2	0	0	0	0	0	0
ζ_8	0.75	0.75	0.5	1	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
ζ_9	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{10}	1	1	1	1	1	1	1	1	1	1	1	1	1
ν_1 (eV)	-72.03287	-35.12015	-111.24473	-30.19634	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214
ν_2 (eV)	26.02344	23.87467	9.50874	38.97278	25.78002	12.87680	9.33352	9.33352	9.33352	9.33352	9.33352	9.33352	9.33352
ν_3 (eV)	21.95990	10.48582	42.82081	7.37432	32.33914	21.06675	10.48582	6.77464	6.77464	6.77464	6.77464	6.77464	6.77464
ν_4 (eV)	-10.97995	-5.24291	-21.41040	-3.68716	-16.26937	-10.33337	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732
ν_5 (eV)	-14.63489	-14.63489	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
ΔE_{HOMO} (eV)	0	0	-2.69893	0	0	0	0	0	0	0	0	0	0
E_1 (eV)	-14.63489	-14.63489	2.69893	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
E_2 (eV)	-49.66493	-31.63533	-63.27074	-31.63533	-67.69431	-49.66493	-31.63533	-31.63533	-31.63533	-31.63533	-31.63533	-31.63533	-31.63533
E_3 (eV)	0	0	-2.69893	-1.85836	0	0	0	-1.85836	-1.85836	-1.44915	-1.44915	-1.44915	-1.44915
E_4 (eV)	-49.66493	-31.63533	-65.56966	-33.49373	-67.69431	-49.66493	-31.63533	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373
ω (10^3 rad/s)	25.2077	24.1759	59.4034	23.3291	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	15.4846	9.43699	9.43699
E_5 (eV)	-0.25493	-0.24966	-0.40804	-0.25966	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
E_6 (eV)	0.35532	0.21077	0.13800	0.35532	0.35532	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.12312	0.12312
E_7 (eV)	-0.07727	-0.07200	-0.30266	-0.19066	-0.22757	-0.14502	-0.07200	-0.10359	-0.10359	-0.15924	-0.10359	-0.10260	-0.10260
E_8 (eV)	0.14803	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E_9 (eV)	-49.61948	-31.70737	-66.57498	-33.68439	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732
E_{HOMO} (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
E_{LUMO} (eV)	-13.59844	-13.59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{\text{HOMO-LUMO}}$ (eV)	7.83968	3.47404	7.80660	4.41461	12.40186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.67128	3.91734

Table 15.91. The total bond energies of alkyl aldehydes calculated using the functional group composition and the energies of Table 15.90 compared to the experimental values [3].

Formula	CH_2 (i)	CH (i)	$\text{C}=\text{O}$ Group	$\text{C}-\text{O}(\text{O})\text{H}$ Group	CH_2 (ii)	CH (ii)	$\text{C}-\text{C}$ (a)	$\text{C}-\text{C}$ (b)	$\text{C}-\text{C}$ (c)	$\text{C}-\text{C}$ (d)	$\text{C}-\text{C}$ (e)	$\text{C}-\text{C}$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_2O	0	0	0	0	0	0	0	0	0	0	0	0	13.54028	13.635	0.00035
CH_3O	0	1	1	1	0	0	0	0	0	0	0	0	28.18711	28.198	0.00039
CH_2O_2	0	1	1	1	0	0	0	0	0	0	0	0	40.34481	40.345	0.00000
CH_3O_2	0	1	1	1	2	0	0	0	0	0	0	0	52.50251	52.491	-0.00022
CH_2O_3	0	1	1	1	3	0	0	0	0	0	0	0	64.66631	64.664	0.00001
CH_3O_3	0	1	1	1	4	0	0	0	0	0	0	0	76.83016	76.830	0.00000
CH_2O_4	0	1	1	1	5	0	0	0	0	0	0	0	88.99461	88.942	-0.00038
CH_3O_4	0	1	1	1	6	0	0	0	0	0	0	0	101.15817	101.179	0.00045
$\text{C}_2\text{H}_5\text{O}$	0	1	2	2	4	1	3	3	3	3	3	3	101.20587	101.259	0.00033

Table 15.52. The bond angle parameters of alkyl aldehydes and experimental values [1]. In the calculation of θ_i , the parameters from the preceding angle were used. E_p is $E_p(\text{atom} - \text{atom}, \text{exp}, \text{AO})$.

Atoms of Angle	$2c_1$ Bond 1 (α_1)	$2c_2$ Bond 2 (α_2)	$2c_3$ Third Atom (α_3)	E_p Atom 1 Hybridization Designation (Table 15.3.A)	E_p Atom 2 Hybridization Designation (Table 15.3.A)	C_1 Atom 1	C_2 Atom 2	C_3 Atom 3	ζ	E_p (eV)	θ_1 ($^\circ$)	θ_2 ($^\circ$)	θ_3 ($^\circ$)	Cal. θ ($^\circ$)	Exp. θ ($^\circ$)
$\angle HC^*H$ (C^*, H, O) (i)	2.09122	2.09132	3.5317	H	H	0.83708	1	1	0.75	0				116.87	116.5 (formaldehyde)
$\angle C_1C_2H$	2.86175	2.11323	4.2269	C_p	1	0.86339	0.91771	0.75	0.75	0				115.52	115.3 (acetaldehyde)
$\angle C_1C_2O$	2.86175	2.27934	4.5826	C_p	0	0.81549	0.83393 (Eq. 15.149)	1	1	-1.65376				123.70	124.1 (acetone)
$\angle HC^*H$ Methane	2.11106	2.11106	3.4252	H	H	0.86359	1	1	0.75	0				108.44	107 (propane)
$\angle C_1C_2C_3$											69.51			110.49	112 (propane) 110.8 (butane) 110.8 (isobutane)
$\angle C_1C_2H$											69.51			110.49	111.4 (acetone)
$\angle HC^*H$	2.09711	2.09711	3.4252	H	H	0.86359	1	1	0.75	0				109.50	109.3 (acetaldehyde)
$\angle C_1C_2C_3$											70.56			109.44	
$\angle C_1C_2C_3$											70.56			109.44	
$\angle C_1C_2C_3$	2.91547	2.91547	4.7958	C_p	C_p	0.81549	0.81549	1	1	-1.83316				110.67	110.8 (acetone)
$\angle C_1C_2H$	2.91547	2.11323	4.1633	C_p	C_p	0.81549	0.91771	0.75	0.75	0				110.76	
$\angle C_1C_2H$	2.91547	2.09711	4.1633	C_p	C_p	0.81549	0.91771	0.75	0.75	0				111.27	111.4 (acetone)
$\angle C_1C_2C_3$	2.90227	2.90227	4.7958	C_p	C_p	0.81549	0.91771	0.75	0.75	-1.83316				111.27	111.4 (acetone)
$\angle C_1C_2C_3$											72.50			109.50	

KETONES ($C_nH_{2n}O$, $n=1,2,3,4,5\ldots\infty$)

The alkyl ketones, $C_nH_{2n}O$, each have a $C=O$ moiety that comprises a functional group. Each of the two single bonds of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. The alkyl portion of the alkyl ketone may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in ketones are equivalent to those in branched-chain alkanes.

The $C=O$ and $C-C(O)$ groups are solved by hybridizing the $2s$ and $2p$ AOs of each C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO or between two $C2sp^3$ HOs, respectively, to form a MO permits each participating orbital to decrease in radius and energy. In alkyl ketones, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C, 2sp^3) = -14.63489 \text{ eV}$ (Eq. (15.25)) and the O AO has an energy of $E(O) = -13.61806 \text{ eV}$. To meet the equipotential condition of the union of the $C=O$ H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C=O$ -bond MO given by Eq. (15.114) is $c_2(C2sp^3HO \text{ to } O) = 0.85395$. The unpaired electrons created by bond breakage of the double $C=O$ bond requires that two times the $O2p$ AO magnetic energy E_{mag} (Eq. (15.60)) be subtracted from the total energy to give $E_D(Grp) \text{ (eV)}$ for $C=O$.

As in the case with aldehydes, $E_T(atom-atom,msp^3.AO)$ of the $C=O$ -bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is -2.69893 eV which is an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the O atom. It is given as a linear combination of

the energy contributions corresponding to a double bond, -1.13379 eV (Eq. (14.247)), and a triple bond, -1.56513 eV (Eq. (14.342)). The triple bond contribution includes the $C2sp^3$ HO electron of the $C-C(O)$ bond in addition to the pair involved directly in the double bond with O . Consequently, $E_T(\text{atom-atom}, msp^3.AO)$ of the $C-C(O)$ -bond MO is -1.44915 eV ,
 5 corresponding to the energy contributions of the two $C2sp^3$ HOs to the single bond that are equivalent to those of methyl groups, -0.72457 eV (Eq. (14.151)). Since there are two $C-C(O)$ bonds in ketones versus one in aldehydes, $C_{1o} = C_1$ in Eq. (15.52) for each $C-C(O)$ ketone bond.

The symbols of the functional groups of alkyl ketones are given in Table 15.93. The
 10 geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.55)) parameters of alkyl ketones are given in Tables 15.94, 15.95, and 15.96, respectively. The total energy of each alkyl ketone given in Table 15.97 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.96 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by
 15 bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(\text{Group})$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl ketones determined using Eqs. (15.79-15.108) are given in Table 15.98.

Table 15.93. The symbols of functional groups of alkyl ketones.

Functional Group	Group Symbol
$C=O$	$C=O$
$C-C(O)$	$C-C(O)$
CH_3 group	$C-H (CH_3)$
CH_2 group	$C-H (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.94. The geometrical bond parameters of alkyl ketones and experimental values [1].

Parameter	C=O Group	C-H (CH ₃) Group	C-H (CH ₂) Group	C-H (CH ₂) Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
σ (°)	1.312172	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
σ' (°)	1.14550	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length 2 σ' (Å)	1.21235	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length 1.219 (2-butanone) (Å)	1.213 (acetone) 1.219 (2-butanone)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
Δ (°)	0.64002	1.46439	1.27295	1.29269	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
σ	0.69887	0.63180	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.95. The MO to HO intercept geometrical bond parameters of alkyl ketones. R, R', R'' are H or alkyl groups. E_p is $E_p(\text{atom} - \text{atom}, \text{map}^1 \text{AO})$.

Bond	Atom	E_p (eV) Bond 1	E_p (eV) Bond 2	E_p (eV) Bond 3	E_p (eV) Bond 4	Final Total Energy C2Zp ¹ (eV)	r_{map} (°)	r_{map} (°)	E_{residual} (eV) Final	E (C2Zp ¹) (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (°)	d_2 (°)
$R'C_1H_2(R'C_1H_2)C_2=O$	O	-1.4046	0	0	0	-154.41430	0.91771	0.84115	-16.17521	-17.43130	136.09	43.91	65.72	0.53955	0.60995
$R'C_1H_2(R'C_1H_2)C_2=O$	C'	-1.4046	-0.72458	-0.72458	0	-154.41430	0.91771	0.77199	-17.62437	-17.43130	133.02	46.98	61.86	0.61878	0.52672
$H_2C_2-C_1(O)(R')$	C'	-0.72458	0	0	0	-153.24026	0.91771	0.87495	-15.53033	-15.23946	73.62	106.38	34.98	1.67762	0.346675
$RH_2C_2-H_2C_2-C_1(O)(R')$	C'	-0.72458	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.23865	67.40	112.60	31.36	1.74821	0.31734
$C'-H$ (CH ₃)	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.31	41.48	1.23564	0.18708
$C'-H$ (CH ₂)	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	32.84	1.34886	0.32933
$H_2C_2C_1H_2C_2H_2$ (C-C (a))	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.43244	61.10	118.90	31.37	1.42988	0.37326
$H_2C_2C_1H_2C_2H_2$ (C-C (b))	C'	-0.92918	0	0	0	-153.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$R-H_2C_2C_1H_2C_2H_2(R')H_2C_2H_2$ (C-C (c))	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_2C_1H_2C_2H_2(R')H_2C_2H_2$ (C-C (d))	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.43244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_2C_1H_2C_2H_2(R')H_2C_2H_2$ (C-C (e))	C'	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$R-H_2C_2C_1H_2C_2H_2(R')H_2C_2H_2$ (C-C (f))	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.43244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_2C_1H_2C_2H_2(R')H_2C_2H_2$ (C-C (g))	C'	-0.72457	-0.72457	-0.72457	-0.72457	-154.31399	0.91771	0.76763	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49258
$R-H_2C_2C_1H_2C_2H_2(R')H_2C_2H_2$ (C-C (h))	C'	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$R-H_2C_2C_1H_2C_2H_2(R')H_2C_2H_2$ (C-C (i))	C'	-0.72457	-0.72457	-0.72457	-0.72457	-154.31399	0.91771	0.76763	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49258

Table 15.96. The energy parameters (eV) of functional groups of alkyl ketones.

Parameters	C=O Group	C=C(O) Group	CH ₃ Group	CH ₂ Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
η_1	2	1	3	2	1	1	1	1	1	1	1
η_2	0	0	2	1	0	0	0	0	0	0	0
η_3	0	0	0	0	0	0	0	0	0	0	0
ζ_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
ζ_2	1	1	1	1	1	1	1	1	1	1	1
ζ_3	1	1	1	1	1	1	1	1	1	1	1
ζ_4	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
ζ_5	2	0	0	1	1	0	0	0	1	1	0
ζ_6	4	2	1	1	1	2	2	2	2	2	2
ζ_7	0	0	0	2	1	0	0	0	0	0	0
ζ_8	0.5	1	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
ζ_9	1	1	1	1	1	1	1	1	1	1	1
ζ_{10}	-109.17602	-30.19634	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214
ζ_{11}	23.75521	9.50874	38.92728	25.78002	12.87680	9.3352	9.3352	9.3352	9.3352	9.3352	9.3352
ζ_{12}	41.60126	7.37432	32.33914	21.06875	10.48582	6.77464	6.77464	6.77464	6.77464	6.77464	6.77464
ζ_{13}	-20.80063	-3.68716	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732
ζ_{14}	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
ΔE_{HOMO} (eV)	-1.34946	0	0	0	0	0	0	0	0	0	0
E_{HOMO} (eV)	1.34946	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
E_{LUMO} (eV)	-63.27071	-31.63534	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537
$E_{\text{HOMO-LUMO}}$ (eV)	-2.69803	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_{\text{HOMO-LUMO}}$ (eV)	-65.56966	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω (10 ⁶ rad/s)	57.0928	16.4962	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.43699	9.43699
E_{HOMO} (eV)	37.57947	10.85807	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.21159	6.21159
E_{LUMO} (eV)	-0.40003	-0.21568	-0.25552	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16515	-0.16515
$E_{\text{HOMO-LUMO}}$ (eV)	0.21462	0.14655	0.35532	0.35532	0.35532	0.2312	0.2312	0.09944	0.2312	0.2312	0.2312
$E_{\text{HOMO-LUMO}}$ (eV)	-0.29272	-0.14240	-0.22757	-0.14502	-0.07200	-0.10359	-0.07200	-0.15924	-0.10359	-0.10359	-0.10359
$E_{\text{HOMO-LUMO}}$ (eV)	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\text{HOMO-LUMO}}$ (eV)	-66.55510	-33.22692	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.24376	-33.59732	-33.18712	-33.18712
$E_{\text{HOMO-LUMO}}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{\text{HOMO-LUMO}}$ (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{\text{HOMO-LUMO}}$ (eV)	7.78672	3.95714	12.49186	7.83016	3.32601	4.32754	4.32754	3.97398	4.17951	3.62128	3.91734

Table 15.97. The total bond energies of alkyl ketones calculated using the functional group composition and the energies of Table 15.96 compared to the experimental values E_{exp} that is subtracted from the weighted sum of the $E_{g,exp}$ (eV) values based on composition is given by (15.57).

Formula	Atoms	C=O Group	C-C(O) Group	CH ₃	CH ₂	CH	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	E_{exp}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₂ H ₄ O	2	2	2	2	0	0	0	0	0	0	0	0	40.672	40.672	40.672	-0.0001
C ₃ H ₆ O	3	2	2	2	1	0	1	0	0	0	0	0	52.842	52.842	52.842	-0.0005
C ₄ H ₈ O	4	2	2	2	2	0	2	0	0	0	0	0	65.0012	65.0012	65.0012	-0.0005
C ₅ H ₁₀ O	5	2	2	2	2	0	2	0	0	0	0	0	77.1604	77.1604	77.1604	-0.0005
C ₆ H ₁₂ O	6	2	2	2	2	0	2	0	0	0	0	0	89.3196	89.3196	89.3196	-0.0005
C ₇ H ₁₄ O	7	2	2	2	2	0	2	0	0	0	0	0	101.4788	101.4788	101.4788	-0.0005
C ₈ H ₁₆ O	8	2	2	2	2	0	2	0	0	0	0	0	113.6380	113.6380	113.6380	-0.0005
C ₉ H ₁₈ O	9	2	2	2	2	0	2	0	0	0	0	0	125.7972	125.7972	125.7972	-0.0005
C ₁₀ H ₂₀ O	10	2	2	2	2	0	2	0	0	0	0	0	137.9564	137.9564	137.9564	-0.0005
C ₁₁ H ₂₂ O	11	2	2	2	2	0	2	0	0	0	0	0	150.1156	150.1156	150.1156	-0.0005
C ₁₂ H ₂₄ O	12	2	2	2	2	0	2	0	0	0	0	0	162.2748	162.2748	162.2748	-0.0005
C ₁₃ H ₂₆ O	13	2	2	2	2	0	2	0	0	0	0	0	174.4340	174.4340	174.4340	-0.0005
C ₁₄ H ₂₈ O	14	2	2	2	2	0	2	0	0	0	0	0	186.5932	186.5932	186.5932	-0.0005
C ₁₅ H ₃₀ O	15	2	2	2	2	0	2	0	0	0	0	0	198.7524	198.7524	198.7524	-0.0005
C ₁₆ H ₃₂ O	16	2	2	2	2	0	2	0	0	0	0	0	210.9116	210.9116	210.9116	-0.0005
C ₁₇ H ₃₄ O	17	2	2	2	2	0	2	0	0	0	0	0	223.0708	223.0708	223.0708	-0.0005
C ₁₈ H ₃₆ O	18	2	2	2	2	0	2	0	0	0	0	0	235.2300	235.2300	235.2300	-0.0005
C ₁₉ H ₃₈ O	19	2	2	2	2	0	2	0	0	0	0	0	247.3892	247.3892	247.3892	-0.0005
C ₂₀ H ₄₀ O	20	2	2	2	2	0	2	0	0	0	0	0	259.5484	259.5484	259.5484	-0.0005
C ₂₁ H ₄₂ O	21	2	2	2	2	0	2	0	0	0	0	0	271.7076	271.7076	271.7076	-0.0005
C ₂₂ H ₄₄ O	22	2	2	2	2	0	2	0	0	0	0	0	283.8668	283.8668	283.8668	-0.0005
C ₂₃ H ₄₆ O	23	2	2	2	2	0	2	0	0	0	0	0	296.0260	296.0260	296.0260	-0.0005
C ₂₄ H ₄₈ O	24	2	2	2	2	0	2	0	0	0	0	0	308.1852	308.1852	308.1852	-0.0005
C ₂₅ H ₅₀ O	25	2	2	2	2	0	2	0	0	0	0	0	320.3444	320.3444	320.3444	-0.0005
C ₂₆ H ₅₂ O	26	2	2	2	2	0	2	0	0	0	0	0	332.5036	332.5036	332.5036	-0.0005
C ₂₇ H ₅₄ O	27	2	2	2	2	0	2	0	0	0	0	0	344.6628	344.6628	344.6628	-0.0005
C ₂₈ H ₅₆ O	28	2	2	2	2	0	2	0	0	0	0	0	356.8220	356.8220	356.8220	-0.0005
C ₂₉ H ₅₈ O	29	2	2	2	2	0	2	0	0	0	0	0	368.9812	368.9812	368.9812	-0.0005
C ₃₀ H ₆₀ O	30	2	2	2	2	0	2	0	0	0	0	0	381.1404	381.1404	381.1404	-0.0005
C ₃₁ H ₆₂ O	31	2	2	2	2	0	2	0	0	0	0	0	393.2996	393.2996	393.2996	-0.0005
C ₃₂ H ₆₄ O	32	2	2	2	2	0	2	0	0	0	0	0	405.4588	405.4588	405.4588	-0.0005
C ₃₃ H ₆₆ O	33	2	2	2	2	0	2	0	0	0	0	0	417.6180	417.6180	417.6180	-0.0005
C ₃₄ H ₆₈ O	34	2	2	2	2	0	2	0	0	0	0	0	429.7772	429.7772	429.7772	-0.0005
C ₃₅ H ₇₀ O	35	2	2	2	2	0	2	0	0	0	0	0	441.9364	441.9364	441.9364	-0.0005
C ₃₆ H ₇₂ O	36	2	2	2	2	0	2	0	0	0	0	0	454.0956	454.0956	454.0956	-0.0005
C ₃₇ H ₇₄ O	37	2	2	2	2	0	2	0	0	0	0	0	466.2548	466.2548	466.2548	-0.0005
C ₃₈ H ₇₆ O	38	2	2	2	2	0	2	0	0	0	0	0	478.4140	478.4140	478.4140	-0.0005
C ₃₉ H ₇₈ O	39	2	2	2	2	0	2	0	0	0	0	0	490.5732	490.5732	490.5732	-0.0005
C ₄₀ H ₈₀ O	40	2	2	2	2	0	2	0	0	0	0	0	502.7324	502.7324	502.7324	-0.0005
C ₄₁ H ₈₂ O	41	2	2	2	2	0	2	0	0	0	0	0	514.8916	514.8916	514.8916	-0.0005
C ₄₂ H ₈₄ O	42	2	2	2	2	0	2	0	0	0	0	0	527.0508	527.0508	527.0508	-0.0005
C ₄₃ H ₈₆ O	43	2	2	2	2	0	2	0	0	0	0	0	539.2100	539.2100	539.2100	-0.0005
C ₄₄ H ₈₈ O	44	2	2	2	2	0	2	0	0	0	0	0	551.3692	551.3692	551.3692	-0.0005
C ₄₅ H ₉₀ O	45	2	2	2	2	0	2	0	0	0	0	0	563.5284	563.5284	563.5284	-0.0005
C ₄₆ H ₉₂ O	46	2	2	2	2	0	2	0	0	0	0	0	575.6876	575.6876	575.6876	-0.0005
C ₄₇ H ₉₄ O	47	2	2	2	2	0	2	0	0	0	0	0	587.8468	587.8468	587.8468	-0.0005
C ₄₈ H ₉₆ O	48	2	2	2	2	0	2	0	0	0	0	0	599.0060	599.0060	599.0060	-0.0005
C ₄₉ H ₉₈ O	49	2	2	2	2	0	2	0	0	0	0	0	611.1652	611.1652	611.1652	-0.0005
C ₅₀ H ₁₀₀ O	50	2	2	2	2	0	2	0	0	0	0	0	623.3244	623.3244	623.3244	-0.0005
C ₅₁ H ₁₀₂ O	51	2	2	2	2	0	2	0	0	0	0	0	635.4836	635.4836	635.4836	-0.0005
C ₅₂ H ₁₀₄ O	52	2	2	2	2	0	2	0	0	0	0	0	647.6428	647.6428	647.6428	-0.0005
C ₅₃ H ₁₀₆ O	53	2	2	2	2	0	2	0	0	0	0	0	659.8020	659.8020	659.8020	-0.0005
C ₅₄ H ₁₀₈ O	54	2	2	2	2	0	2	0	0	0	0	0	671.9612	671.9612	671.9612	-0.0005
C ₅₅ H ₁₁₀ O	55	2	2	2	2	0	2	0	0	0	0	0	684.1204	684.1204	684.1204	-0.0005
C ₅₆ H ₁₁₂ O	56	2	2	2	2	0	2	0	0	0	0	0	696.2796	696.2796	696.2796	-0.0005
C ₅₇ H ₁₁₄ O	57	2	2	2	2	0	2	0	0	0	0	0	708.4388	708.4388	708.4388	-0.0005
C ₅₈ H ₁₁₆ O	58	2	2	2	2	0	2	0	0	0	0	0	720.5980	720.5980	720.5980	-0.0005
C ₅₉ H ₁₁₈ O	59	2	2	2	2	0	2	0	0	0	0	0	732.7572	732.7572	732.7572	-0.0005
C ₆₀ H ₁₂₀ O	60	2	2	2	2	0	2	0	0	0	0	0	744.9164	744.9164	744.9164	-0.0005
C ₆₁ H ₁₂₂ O	61	2	2	2	2	0	2	0	0	0	0	0	757.0756	757.0756	757.0756	-0.0005
C ₆₂ H ₁₂₄ O	62	2	2	2	2	0	2	0	0	0	0	0	769.2348	769.2348	769.2348	-0.0005
C ₆₃ H ₁₂₆ O	63	2	2	2	2	0	2	0	0	0	0	0	781.3940	781.3940	781.3940	-0.0005
C ₆₄ H ₁₂₈ O	64	2	2	2	2	0	2	0	0	0	0	0	793.5532	793.5532	793.5532	-0.0005
C ₆₅ H ₁₃₀ O	65	2	2	2	2	0	2	0	0	0	0	0	805.7124	805.7124	805.7124	-0.0005
C ₆₆ H ₁₃₂ O	66	2	2	2	2	0	2	0	0	0	0	0	817.8716	817.8716	817.8716	-0.0005
C ₆₇ H ₁₃₄ O	67	2	2	2	2	0	2	0	0	0	0	0	830.0308	830.0308	830.0308	-0.0005
C ₆₈ H ₁₃₆ O	68	2	2	2	2	0	2	0	0	0	0	0	842.1900	842.1900	842.1900	-0.0005
C ₆₉ H ₁₃₈ O	69	2	2	2	2	0	2	0	0	0	0	0	854.3492	854.3492	854.3492	-0.0005
C ₇₀ H ₁₄₀ O	70	2	2	2	2	0	2	0	0	0	0	0	866.5084	866.5084	866.5084	-0.0005
C ₇₁ H ₁₄₂ O	71	2	2	2	2	0	2	0	0	0	0	0	878.6676	878.6676	878.6676	-0.0005
C ₇₂ H ₁₄₄ O	72	2	2	2	2	0	2	0	0	0	0	0	890.8268	890.8268	890.8268	-0.0005
C ₇₃ H ₁₄₆ O	73	2	2	2	2	0	2	0	0	0	0	0	902.9860	902.9860	902.9860	-0.0005
C ₇₄ H ₁₄₈ O	74	2	2	2	2	0	2	0	0	0	0	0	915.1452	915.1452	915.1452	-0.0005
C ₇₅ H ₁₅₀ O	75	2	2	2	2	0	2	0	0	0	0	0	927.3044	927.3044	927.3044	-0.0005
C ₇₆ H ₁₅₂ O	76	2	2	2	2	0	2	0	0	0	0	0	939.4636	939.4636	939.4636	-0.0005
C ₇₇ H ₁₅₄ O	77	2	2	2	2	0	2	0	0	0	0	0	951.6228	951.6228	951.6228	-0.0005
C ₇₈ H ₁₅₆ O	78	2	2	2	2	0	2	0	0	0	0	0	963.7820	963.7820	963.7820	-0.0005
C ₇₉ H ₁₅₈ O	79	2	2	2	2	0	2	0	0	0	0	0	975.9412	975.9412	975.9412	-0.0005
C ₈₀ H ₁₆₀ O	80	2	2	2	2	0	2	0	0	0	0	0	988.1004	988.1004	988.1004	-0.0005
C ₈₁ H ₁₆₂ O	81	2	2	2	2	0	2	0	0	0	0	0	1000.2596	100		

CARBOXYLIC ACIDS ($C_nH_{2n}O_2$, $n = 1, 2, 3, 4, 5, \dots, \infty$)

The alkyl carboxylic acids, $C_nH_{2n}O_2$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. Formic acid has a $HC=O$ moiety that comprises a more stable $C=O$ functional group and a CH functional group. All carboxylic acids further comprise a $C-OH$ moiety that comprises $C-O$ and OH functional groups. The alkyl portion of the alkyl carboxylic acid may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acids are equivalent to those in branched-chain alkanes.

The CH functional group was solved in the Hydrogen Carbide (CH) section except that the energy of the $C-H$ MO is matched to the carbon-atom contribution to $\Delta E_{H_2MO}(AO/HO)$ and $E_r(atom-atom, msp^3.AO)$ of the $C-O$ group. The alkyl carboxylic acid $C=O$ and $C-C(O)$ groups are equivalent to those given in the Aldehydes section except that $\bar{E}_{K_{vib}}$ is that of a carboxylic acid. The formic acid $C=O$ group is solved equivalently to that of the alkyl carboxylic acid group, except that $\Delta E_{H_2MO}(AO/HO)$ and $E_r(atom-atom, msp^3.AO)$ correspond to a 25% increase in the donation of charge density from the orbitals of the atoms to the $C=O$ MO due to the presence of a H bound to the carbonyl carbon. Also, $\bar{E}_{K_{vib}}$ is that corresponding to formic acid. The $C-O$ and OH groups are equivalent to those of alkyl alcohols given in the corresponding section except that the energy of the $C-O$ MO is matched to that of the $C=O$ group and $\bar{E}_{K_{vib}}$ is that of a carboxylic acid. $\Delta E_{H_2MO}(AO/HO)$ of the $C-O$ group is equal to $E_r(atom-atom, msp^3.AO)$ of the alkyl $C=O$ group in order to match the energies of the corresponding MOs.

As in the case with aldehydes and ketones, $E_r(atom-atom, msp^3.AO)$ of the $C=O$ -bond MO in Eq. (15.52) of alkyl carboxylic acids due to the charge donation from the C and O

atoms to the MO is -2.69893 eV which is an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the carbonyl O atom. It is given as a linear combination of the energy contributions corresponding to a double bond, -1.13379 eV (Eq. (14.247)), and a triple bond, -1.56513 eV (Eq. (14.342)). The triple bond contribution includes the energy match of the carbonyl $C2sp^3$ HO electron with the O of the $C-O$ -bond MO in addition to the pair involved directly in the double bond with the carbonyl O .

$E_T(\text{atom} - \text{atom}, msp^3.AO)$ of the formic acid $C=O$ -bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is -3.58557 eV . This is also an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the carbonyl O atom. It is given as a linear combination of the energy contributions corresponding to a triple bond, -1.56513 eV (Eq. (14.342)), and a quadruple bond, -2.02043 eV (Eqs. (15.18-15.21) with $s=4$) where the bond order components are increased by an integer over that of alkyl carboxylic acids due to the presence of a H bound to the carbonyl carbon.

$E_T(\text{atom} - \text{atom}, msp^3.AO)$ of the carboxylic acid $C-C(O)$ group is equivalent to that of alkanes and aldehydes, -1.85836 eV , where both energy contributions are given by Eq. (14.513). It is based on the energy match between the $C2sp^3$ HOs of the carboxylic acid. As in the case of aldehydes, $C_{1o} = 2C_1$ in Eq. (15.52).

$E_T(\text{atom} - \text{atom}, msp^3.AO)$ of the carboxylic acid $C-O$ group is equivalent to that of alkyl alcohols, -1.85836 eV . It is based on the energy match between the O AO and the $C2sp^3$ HO of a methylene group (the maximum hybridization for a single bond) where both energy contributions are given by Eq. (14.513). $E_T(\text{atom} - \text{atom}, msp^3.AO)$ of the $C-O$ group matches that of the $C-C(O)$ group.

The symbols of the functional groups of alkyl carboxylic acids are given in Table 15.99. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acids are given in Tables 15.100, 15.101, and 15.102, respectively. The total energy of each alkyl carboxylic acid given in Table 15.103 was calculated as the sum over the integer multiple of each $E_D(\text{group})$ of Table 15.102 corresponding to functional-group composition of the molecule. For each set of unpaired

electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl carboxylic acids determined using Eqs. (15.79-15.108) are given in Table 15.104.

Table 15.99. The symbols of functional groups of alkyl carboxylic acids.

Functional Group	Group Symbol
CH (formic acid) group	$C-H$ (i)
C-C(O)	$C-C(O)$
C=O (formic acid)	$C=O$ (i)
C=O (alkyl carboxylic acid)	$C=O$ (ii)
(O)C-O	$C-O$
OH group	OH
CH_3 group	$C-H$ (CH_3)
CH_2 group	$C-H$ (CH_2)
CH (alkyl) group	$C-H$ (ii)
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.100 The geometrical bond parameters of alkyl carboxylic acids and experimental values [1].

Parameter	C-H (f)	C=O (f)	C=O (g)	C=O (h)	OH Group	C-H (CH ₃) Group	C-H (CH ₂) Group	C-H (CH) Group	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)
σ (a)	1.61341	1.20799	1.24907	1.24907	1.36430	1.46122	1.57465	1.72499	1.210725	1.210725	1.210725	1.210725	1.210725	1.210725
σ (a)	1.03711	1.13013	1.13977	1.13977	0.91808	1.00836	1.08661	1.45744	1.45744	1.45744	1.45744	1.45744	1.45744	1.45164
Bond Length														
$2c$ (A)	1.09763	1.20343	1.20628	1.20628	0.971651	1.10974	1.11713	1.11827	1.44380	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (A)	1.097	1.202 (formic acid)	1.214 (acetic acid)	1.214 (acetic acid)	0.972 (formic acid)	1.107 (C-H propane)	1.107 (C-H propane)	1.122 (isobutane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.531 (butane)	1.531 (butane)
h (a)	0.22591	0.61267	0.67331	0.67331	0.86925	1.27295	1.29569	1.29924	1.34616	1.54616	1.54616	1.54616	1.54616	1.52750
h (a)	0.22591	0.61267	0.67331	0.67331	0.86925	1.27295	1.29569	1.29924	1.34616	1.54616	1.54616	1.54616	1.54616	1.52750
h (a)	0.22591	0.61267	0.67331	0.67331	0.86925	1.27295	1.29569	1.29924	1.34616	1.54616	1.54616	1.54616	1.54616	1.52750
h (a)	0.22591	0.61267	0.67331	0.67331	0.86925	1.27295	1.29569	1.29924	1.34616	1.54616	1.54616	1.54616	1.54616	1.52750
h (a)	0.22591	0.61267	0.67331	0.67331	0.86925	1.27295	1.29569	1.29924	1.34616	1.54616	1.54616	1.54616	1.54616	1.52750
h (a)	0.22591	0.61267	0.67331	0.67331	0.86925	1.27295	1.29569	1.29924	1.34616	1.54616	1.54616	1.54616	1.54616	1.52750
h (a)	0.22591	0.61267	0.67331	0.67331	0.86925	1.27295	1.29569	1.29924	1.34616	1.54616	1.54616	1.54616	1.54616	1.52750
h (a)	0.22591	0.61267	0.67331	0.67331	0.86925	1.27295	1.29569	1.29924	1.34616	1.54616	1.54616	1.54616	1.54616	1.52750
h (a)	0.22591	0.61267	0.67331	0.67331	0.86925	1.27295	1.29569	1.29924	1.34616	1.54616	1.54616	1.54616	1.54616	1.52750
h (a)	0.22591	0.61267	0.67331	0.67331	0.86925	1.27295	1.29569	1.29924	1.34616	1.54616	1.54616	1.54616	1.54616	1.52750
h (a)	0.22591	0.61267	0.67331	0.67331	0.86925	1.27295	1.29569	1.29924	1.34616	1.54616	1.54616	1.54616	1.54616	1.52750
h (a)	0.22591	0.61267	0.67331	0.67331	0.86925	1.27295	1.29569	1.29924	1.34616	1.54616	1.54616	1.54616	1.54616	1.52750
h (a)	0.22591	0.61267	0.67331	0.67331	0.86925	1.27295	1.29569	1.29924	1.34616	1.54616	1.54616	1.54616	1.54616	1.52750
h (a)	0.22591	0.61267	0.67331	0.67331	0.86925	1.27295	1.29569	1.29924	1.34616	1.54616	1.54616	1.54616	1.54616	1.52750
h (a)	0.22591	0.61267	0.67331	0.67331	0.86925	1.27295	1.29569	1.29924						

to 1.1–1.6 m; TL = 1.0 m; 10 mm increments of all but caudal fin (AD). E is $E_{\text{caudal}} - a(\text{cm, mm}, AD)$.

Table 15. (10). The MO to HO intercept geometrical bond parameters of alkyl carboxylic acids. R, R', R'' are H or CH_3 groups. Σ_1 to Σ_6 (linear = zeroing out Σ_1).

Bond	Atom	E_c (eV)	E_c (eV)	E_c (eV)	E_c (eV)	Final Energy '2ap' (eV)	E_{Final} (eV)	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (Å)	d_2 (Å)	d_3 (Å)
$RC_1(O)O-H$	O	-0.92918	0	0	0	0	-15.75493	115.09	64.91	64.12	0.51182	0.56205	
	O	-0.92918	0	0	0	0	-15.75493	101.22	78.68	49.58	1.14965	0.09593	
$HC_1(O)-OH$	O	-0.92918	0	0	0	-154.33766	-17.54772	93.94	80.06	43.24	1.30586	0.00329	
	O	-0.92918	0	0	0	-154.33766	-17.54772	101.22	78.68	48.58	1.17055	0.16950	
$RC_1(O)O-H$	O	-0.92918	0	0	0	0	-16.03358	91.96	86.64	41.90	1.29118	0.02378	
	O	-0.92918	0	0	0	0	-16.03358	137.10	42.80	63.45	0.39393	0.99978	
$HC_1(O)O-H$	O	-0.92918	0	0	0	0	-16.61833	135.24	44.76	63.02	0.38361	0.56053	
	O	-0.92918	0	0	0	0	-16.61833	137.27	42.73	66.31	0.31993	0.61784	
$RC_1(O)O-H$	O	-0.92918	0	0	0	0	-16.17321	133.47	46.53	61.46	0.63072	0.51965	
	O	-0.92918	0	0	0	0	-16.17321	68.89	110.11	36.09	1.30373	0.36662	
$HC_1(O)O-H$	O	-0.92918	0	0	0	0	-17.54772	93.94	80.06	43.24	1.30586	0.00329	
	O	-0.92918	0	0	0	0	-17.54772	101.22	78.68	48.58	1.17055	0.16950	
$RC_1(O)O-H$	O	-0.92918	0	0	0	0	-16.03358	91.96	86.64	41.90	1.29118	0.02378	
	O	-0.92918	0	0	0	0	-16.03358	137.10	42.80	63.45	0.39393	0.99978	
$HC_1(O)O-H$	O	-0.92918	0	0	0	0	-16.61833	135.24	44.76	63.02	0.38361	0.56053	
	O	-0.92918	0	0	0	0	-16.61833	137.27	42.73	66.31	0.31993	0.61784	
$RC_1(O)O-H$	O	-0.92918	0	0	0	0	-16.17321	133.47	46.53	61.46	0.63072	0.51965	
	O	-0.92918	0	0	0	0	-16.17321	68.89	110.11	36.09	1.30373	0.36662	
$HC_1(O)O-H$	O	-0.92918	0	0	0	0	-17.54772	93.94	80.06	43.24	1.30586	0.00329	
	O	-0.92918	0	0	0	0	-17.54772	101.22	78.68	48.58	1.17055	0.16950	
$RC_1(O)O-H$	O	-0.92918	0	0	0	0	-16.03358	91.96	86.64	41.90	1.29118	0.02378	
	O	-0.92918	0	0	0	0	-16.03358	137.10	42.80	63.45	0.39393	0.99978	
$HC_1(O)O-H$	O	-0.92918	0	0	0	0	-16.61833	135.24	44.76	63.02	0.38361	0.56053	
	O	-0.92918	0	0	0	0	-16.61833	137.27	42.73	66.31	0.31993	0.61784	
$RC_1(O)O-H$	O	-0.92918	0	0	0	0	-16.17321	133.47	46.53	61.46	0.63072	0.51965	
	O	-0.92918	0	0	0	0	-16.17321	68.89	110.11	36.09	1.30373	0.36662	
$HC_1(O)O-H$	O	-0.92918	0	0	0	0	-17.54772	93.94	80.06	43.24	1.30586	0.00329	
	O	-0.92918	0	0	0	0	-17.54772	101.22	78.68	48.58	1.17055	0.16950	
$$													

CARBOXYLIC ACID ESTERS ($C_nH_{2n}O_2$, $n = 1, 2, 3, 4, 5 \dots \infty$)

The alkyl carboxylic acid esters, $C_nH_{2n}O_2$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. Formic acid ester has a $HC=O$ moiety that comprises a more stable $C=O$ functional group and a CH functional group. All carboxylic acid esters further comprise a COR moiety that comprises a $C-O$ functional group and three types of $O-R$ functional groups, one for R comprising methyl, one for R comprising an alkyl ester group of a formate, and one for R comprising an alkyl ester group of an alkyl carboxylate. The alkyl portion of the alkyl carboxylic acid ester may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n -alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t -butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t -butyl, and t -butyl to t -butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acid esters are equivalent to those in branched-chain alkanes.

The CH functional group is equivalent to that of formic acid. The alkyl carboxylic acid ester $C=O$ and $C-C(O)$ groups are equivalent to those given in the Carboxylic Acids section. The formic acid ester $C=O$ group is equivalent to that given in the Carboxylic Acids section except that \bar{E}_{Kvb} is that corresponding to a formic acid ester. The $C-O$ group is equivalent to that given in the Carboxylic Acids section except that the parameters corresponding to oscillation of the bond in the transition state, \bar{E}_D (eV) and \bar{E}_{Kvb} , are those of a carboxylic acid ester. As in the case with the alkyl ethers, each $O-C$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the $O-C$ H_2 -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.51) for the $O-C$ -bond MO given by Eq. (15.114) is $c_2(C2sp^3HO \text{ to } O) = 0.85395$.

$E_T(\text{atom-atom}, \text{msp}^3, \text{AO})$ (Eq. (15.52)) of (1) the $C=O$ group of alky carboxylic acid esters, (2) the $C=O$ group of formic acid esters, (3) the alkyl carboxylic acid ester $C-C(O)$ group, and (4) the carboxylic acid ester $C-O$ group are equivalent to those of the corresponding carboxylic acids. The values given in the Carboxylic Acids section are 5 -2.69893 eV , -3.58557 eV , -1.85836 eV , and -1.85836 eV , respectively. $E_T(\text{atom-atom}, \text{msp}^3, \text{AO})$ of the $C-O$ group matches that of the $C-C(O)$ group. Also, as in the case of aldehydes, $C_{1o} = 2C_1$ in Eq. (15.52) for the $C-C(O)$ group.

$E_T(\text{atom-atom}, \text{msp}^3, \text{AO})$ of the $O-C$ -bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is -1.13379 eV for the $O-CH_3$ group of 10 formate and alkyl carboxylates, -1.44915 eV for the $O-R$ group of alkyl carboxylates, and -1.85836 eV for the $O-R$ group of alkyl formates, where R is an alkyl group. Each is based on the energy match between the O AO, initially at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively), the $C2sp^3$ HO of the methyl or alkyl ester 15 group, and the carbonyl carbon. The increasing energy contributions to the single bond correspond to the increasing hybridization of linear combinations of increasing bond order. The energy contributions corresponding to one half of a double bond and those of the methyl-methyl and methylene-methylene bonds are -1.13379 eV (Eq. (14.247)), two times -0.72457 eV (Eq. (14.151)), and two times -0.92918 eV (Eq. (14.513)), respectively.

The symbols of the functional groups of alkyl carboxylic acid esters are given in Table 20 15.105. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid esters are given in Tables 15.106, 15.107, and 15.108, respectively. The total energy of each alkyl carboxylic acid ester given in Table 15.109 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.108 corresponding to functional-group composition of the 25 molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(\text{Group})$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl carboxylic acid esters determined using Eqs. (15.79-15.108) are given in Table 15.110.

Table 15.105. The symbols of functional groups of alkyl carboxylic acid esters.

Functional Group	Group Symbol
CH (formic acid ester) group	$C-H$ (i)
C-C(O)	$C-C(O)$
C=O (formic acid ester)	$C=O$ (i)
C=O (alkyl carboxylic acid ester)	$C=O$ (ii)
(O)C-O	$C-O$
O-CH ₃	$O-C$ (i)
O-R (formic acid ester)	$O-C$ (ii)
O-R (alkyl acid ester)	$O-C$ (iii)
OH group	OH
CH ₃ group	$C-H$ (CH ₃)
CH ₂ group	$C-H$ (CH ₂)
CH (alkyl) group	$C-H$ (ii)
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.105. The geometrical bond parameters of alkyl carboxylic acid esters and experimental values [1].

Parameter	C-H (i) Group	C-C(O) Group	C=O (i) Group	C=O (ii) Group	C-O Group	O-C (i) Group	O-C (ii) Group	O-C (iii) Group	C-H (CH ₃) Group	C-H (CH ₂) Group	C-H (iii) Group	C-C (ii) Group	C-C (iv) Group	C-C (v) Group	C-C (vi) Group	C-C (vii) Group	C-C (viii) Group
σ (a_0)	1.61341	2.04740	1.290799	1.29907	1.73490	1.78255	1.78255	1.80717	1.67122	1.67465	2.12499	2.12499	2.12499	2.10725	2.10725	2.10725	2.10725
σ' (a_0)	1.03711	1.43087	1.13613	1.13977	1.31716	1.35160	1.35160	1.34431	1.04856	1.05553	1.45744	1.45744	1.45744	1.45164	1.45164	1.45164	1.45164
Bond Length $2\sigma'$ (\AA)	1.09763	1.51437	1.20243	1.20628	1.39402	1.43047	1.43047	1.42276	1.10974	1.11713	1.54280	1.54280	1.54280	1.53635	1.53635	1.53635	1.53635
Exp. Bond Length (\AA)	1.101 (methyl formate)	1.520 (acetic acid)	1.206 (methyl formate)	1.214 (acetic acid)	1.393 (avg. methyl formate)	1.393 (avg. methyl formate)	1.393 (avg. methyl formate)	1.393 (avg. methyl formate)	1.107 (methyl formate) 1.107 (C-H propane) 1.117 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
λ, σ' (a_0)	1.23591	1.46439	0.61267	0.62331	1.12915	1.22901	1.22901	1.20776	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.52750	1.52750	1.52750
σ	0.64281	0.69887	0.38018	0.57757	0.73971	0.73986	0.73986	0.74388	0.63150	0.63159	0.65095	0.68600	0.68600	0.68888	0.68888	0.68888	0.68888

Table 15.107. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid esters. R, R', R'' are H or alkyl groups. E_r is $E_r(\text{atom} - \text{atom}, \text{exp}, \text{AO})$.

Bond	Atom	E_r (eV) Bond 1	E_r (eV) Bond 2	E_r (eV) Bond 3	E_r (eV) Bond 4	Final Total Energy C2sp ² (eV)	r_{bond} (Å)	E_{C2sp^2} (eV) Final	E_{C2sp^2} (eV) Final	θ^* (°)	θ_1 (°)	θ_2 (°)	d_1 (Å)	d_2 (Å)
$RC_1(O)O-C_1H_3$ (O-C (i))	O	-0.92018	-0.56690	0	0	-152.16239	1.00000	-16.32183	-16.32183	90.63	89.37	42.70	1.34246	0.00914
$RC_1(O)O-C_1H_3$ (O-C (ii))	C ₁	-0.56690	0	0	0	-152.16239	0.91771	-13.92635	-13.92635	93.01	84.99	45.76	1.27445	0.07716
$HC_1(O)O-C_1H_3$ (O-C (iii))	O	-0.92018	-0.92018	0	0	-153.47405	1.00000	-16.08412	-16.08412	93.09	86.91	43.59	1.29113	0.00939
$HC_1(O)O-C_1H_3$ (O-C (iv))	C ₁	-0.92018	-0.92018	0	0	-153.47405	0.91771	-16.08411	-16.08411	93.09	86.91	43.59	1.29113	0.00939
$RC_1(O)O-C_1H_3$ (O-C (v))	O	-0.92018	-0.92018	0	0	-153.47405	1.00000	-16.07951	-16.07951	91.72	88.28	43.10	1.31931	0.02480
$RC_1(O)O-C_1H_3$ (O-C (vi))	C ₁	-0.92018	-0.92018	0	0	-153.47405	0.91771	-16.07951	-16.07951	91.72	88.28	43.10	1.31931	0.02480
$HC_1(O)O-C_1H_3$ (O-C (vii))	O	-0.92018	-0.92018	0	0	-153.47405	1.00000	-16.32183	-16.32183	98.97	81.03	46.82	1.18716	0.13000
$HC_1(O)O-C_1H_3$ (O-C (viii))	C ₁	-0.92018	-0.92018	0	0	-153.47405	0.91771	-17.54772	-17.54772	93.94	86.06	43.24	1.20386	0.03329
$HC_1(O)O-C_1H_3$ (O-C (ix))	O	-0.92018	-0.92018	0	0	-153.47405	1.00000	-16.08412	-16.08412	97.48	82.52	45.73	1.21100	0.10616
$HC_1(O)O-C_1H_3$ (O-C (x))	C ₁	-0.92018	-0.92018	0	0	-153.47405	0.91771	-17.54772	-17.54772	93.94	86.06	43.24	1.20386	0.03329
$RC_1(O)O-C_1H_3$ (O-C (xi))	O	-0.92018	-0.56690	0	0	-154.33765	1.00000	-16.32183	-16.32183	91.57	81.03	46.82	1.18716	0.13000
$RC_1(O)O-C_1H_3$ (O-C (xii))	C ₁	-0.92018	-0.56690	0	0	-154.33765	0.91771	-18.03358	-18.03358	91.56	88.04	41.90	1.20138	0.03378
$RC_1(O)O-C_1H_3$ (O-C (xiii))	O	-0.92018	-0.73437	0	0	-154.33765	1.00000	-16.47951	-16.47951	91.32	81.68	46.34	1.19766	0.11849
$RC_1(O)O-C_1H_3$ (O-C (xiv))	C ₁	-0.92018	-1.34946	-0.92018	0	-154.33765	0.91771	-18.03358	-18.03358	91.56	88.04	41.90	1.20138	0.03378
$RC_1(O)O-C_1H_3$ (O-C (xv))	O	-0.92018	-1.34946	-0.92018	0	-154.33765	1.00000	-16.47951	-16.47951	137.10	42.90	63.45	0.53635	0.59978
$RC_1(O)O-C_1H_3$ (O-C (xvi))	C ₁	-0.92018	-1.34946	-0.92018	0	-154.33765	0.91771	-17.54772	-17.54772	133.24	44.76	63.02	0.53561	0.53033
$RC_1(O)O-C_1H_3$ (O-C (xvii))	O	-0.92018	-0.92018	-0.92018	0	-154.33765	1.00000	-16.17521	-16.17521	137.27	42.73	66.31	0.53193	0.61784
$RC_1(O)O-C_1H_3$ (O-C (xviii))	C ₁	-0.92018	-0.92018	-0.92018	0	-154.33765	0.91771	-18.03358	-18.03358	133.47	46.53	61.46	0.63972	0.51905
$RC_1(O)O-C_1H_3$ (O-C (xix))	O	-0.92018	-0.92018	-0.92018	0	-154.33765	1.00000	-17.54772	-17.54772	69.89	110.11	36.09	1.30773	0.16662
$RC_1(O)O-C_1H_3$ (O-C (xx))	C ₁	-0.92018	-1.34946	-0.92018	0	-154.33765	0.91771	-18.03358	-18.03358	56.25	122.75	25.37	1.81002	0.41915
$RC_1(O)O-C_1H_3$ (O-C (xxi))	O	-0.92018	-0.92018	-0.92018	0	-154.33765	1.00000	-15.56497	-15.56497	72.27	107.73	34.17	1.69318	0.26501
$RC_1(O)O-C_1H_3$ (O-C (xxii))	C ₁	-0.92018	-0.92018	-0.92018	0	-154.33765	0.91771	-16.08411	-16.08411	63.99	114.01	30.58	1.70270	0.33143
$RC_1(O)O-C_1H_3$ (O-C (xxiii))	O	-0.92018	-0.92018	-0.92018	0	-154.33765	1.00000	-15.56497	-15.56497	77.49	102.51	41.48	1.25564	0.18708
$RC_1(O)O-C_1H_3$ (O-C (xxiv))	C ₁	-0.92018	-0.92018	-0.92018	0	-154.33765	0.91771	-16.08411	-16.08411	68.47	111.53	35.44	1.35486	0.29933

Band	Atom	E_F (eV) Bond 1	E_F (eV) Bond 2	E_F (eV) Bond 3	E_F (eV) Bond 4	Final Total Energy C _{2sp} ² (eV)	r_{C-H} (a_0)	r_{C-C} (a_0)	r_{C-H} (a_0)	$E_{C_{2sp}^2}$ (eV) Final	θ^* (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H$ (H) (H)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.17247	0.91771	0.17247	-17.61330	61.10	118.90	31.37	1.42938	0.37226
$H_2C_2H_2$ (H) (H)	C	-0.92918	0	0	0	-152.4487	0.18339	0.91771	0.18339	-15.75493	63.82	116.18	30.08	1.31879	0.31106
$H_2C_2H_2$ (H) (H)	C	-0.92918	-0.92918	0	0	-153.47466	0.18349	0.91771	0.18349	-16.04112	56.41	123.59	28.06	1.50390	0.45117
$H-H$ (H) (H)	H	-0.92918	-0.92918	-0.92918	0	-154.40324	0.17247	0.91771	0.17247	-17.61330	48.30	131.70	21.90	1.97162	0.51388
$H-H$ (H) (H)	H	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.15189	0.91771	0.15189	-17.92866	48.21	131.70	21.74	1.95734	0.50570
$H-H$ (H) (H)	H	-0.92918	-0.92918	-0.92918	0	-154.40324	0.17247	0.91771	0.17247	-17.61330	48.30	131.70	21.90	1.97162	0.51388
$H-H$ (H) (H)	H	-0.72457	-0.72457	-0.72457	-0.72457	-154.51390	0.16765	0.91771	0.16765	-17.92866	50.04	130.96	22.66	1.94462	0.49298
$H-H$ (H) (H)	H	-0.72457	-0.72457	-0.92918	0	-154.19863	0.18155	0.91771	0.18155	-17.40869	52.78	127.22	24.04	1.52443	0.37279
$H-H$ (H) (H)	H	-0.72457	-0.72457	-0.72457	-0.72457	-154.51390	0.16765	0.91771	0.16765	-17.92866	50.04	130.96	22.66	1.94462	0.49298

Parameters	$C-H$ (i)	$C-D$ (i)	$C=O$ (i)	$C=O$ (ii)	$C-O$	$O-C$ (i)	$O-C$ (ii)	$O-C$ (iii)	CH_2	CH_3	$C-H$ (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)
Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
n_1	1	2	1	2	1	1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	0	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
n_4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.75	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
C_3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
C_4	0.91771	0.91771	0.85395	0.85395	0.85395	0.85395	0.85395	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
C_5	0	2	0	2	0	0	0	0	0	1	1	0	0	1	1	0	0
C_6	1	2	4	4	2	2	2	2	1	1	1	2	2	2	2	2	2
C_7	1	0	0	0	0	0	0	0	3	2	1	0	0	0	0	0	0
C_8	0.75	1	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{10}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
V_1 (eV)	-36.74167	-30.16634	-112.61934	-111.24473	-35.08488	-32.67173	-33.78830	-33.13737	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_2 (eV)	13.11890	9.50874	23.95107	23.97467	10.32068	10.06642	10.19070	10.12105	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
V_3 (eV)	11.38634	7.37432	43.62380	42.82081	10.11150	8.94219	9.47754	9.17839	32.57594	10.08582	6.77464	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_4 (eV)	-5.69317	-5.68716	-21.81195	-21.41040	-5.05575	-4.47110	-4.73877	-4.58695	-16.26657	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_{\text{ion}}^{\text{atom}}(\text{eV})$	-14.63489	-14.63489	0	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{\text{ion}}^{\text{atom}}(\text{eV})$	-0.92918	0	-3.48357	-2.69893	-2.69893	-1.13379	-1.85836	-1.44915	0	0	0	0	0	0	0	0	0
$E_{\text{H}}^{\text{atom}}(\text{eV})$	-13.70371	-14.63489	3.58357	2.69893	-11.93196	-13.50110	-12.77653	-13.18374	-13.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E_{\text{L}}^{\text{atom}}(\text{eV})$	-31.63550	-31.63554	-63.27075	-63.27074	-31.63341	-31.63331	-31.63356	-31.63353	-67.69451	-49.66493	-31.63333	-31.63337	-31.63337	-31.63333	-31.63337	-31.63333	-31.63333
$E_{\text{F}}^{\text{atom}}(\text{eV})$	0	-1.84836	-3.58357	-2.69893	-1.85836	-1.13379	-1.85836	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915</

AMIDES ($C_nH_{2n+1}NO$, $n = 1, 2, 3, 4, 5 \dots \infty$)

The alkyl amides, $C_nH_{2n+1}NO$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. Formamide has a $HC=O$ moiety that comprises a more stable $C=O$ functional group and a CH functional group that is equivalent to that of the CH (i) of aldehydes given in the corresponding section. It is also equivalent to that of the iso- CH group of branched-chain-alkyl portion of the alkyl amide except that E_{mag} (Eq. (15.58)) is not subtracted from $E_D(Grp)$. All amides further comprise a $C-NH_2$ moiety that comprises a NH_2 functional group and two types of $C-N$ functional groups, one for formamide and the other for alkyl amides ($RC(O)NH_2$ where R is alkyl). The alkyl portion of the alkyl amide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in amides are equivalent to those in branched-chain alkanes.

The NH_2 functional group was solved in the Dihydrogen Nitride (NH_2) section except that the energy of the $N-H$ MO is matched to the nitrogen-atom contribution to $\Delta E_{H_2MO}(AO/HO)$ and $E_r(atom-atom,msp^3.AO)$ of the $C-N$ group. Both alkyl amide $C=O$ groups and the $C-C(O)$ group are equivalent to those given in the Carboxylic Acid Esters section except that \bar{E}_{Kvib} of the $C-C(O)$ group is matched to that of an amide. The $C-N$ groups are equivalent to those of alkyl amines given in the corresponding section except that the energy of the $C-N$ MO is matched to that of the $C=O$ group and \bar{E}_{Kvib} is that of an amide. $\Delta E_{H_2MO}(AO/HO)$ of the $C-N$ group is equal to $E_r(atom-atom,msp^3.AO)$ of the alkyl $C=O$ and $C-N$ groups in order to match the energies of the corresponding MOs.

As in the case of primary amines, each $C-N$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of

electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the $C-N$ H_2 -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.52) for the $C-N$ -bond MO given by Eq. (15.114) is $c_2(C2sp^3HO \text{ to } N) = 0.91140$.

5 $E_T(atom - atom, msp^3.AO)$ (Eq. (15.52)) of the $C=O$ group of alky amides and the $C=O$ group of formamide are equivalent to those of the corresponding carboxylic acids and esters. The values given in the Carboxylic Acids section are -2.69893 eV and -3.58557 eV , respectively.

$E_T(atom - atom, msp^3.AO)$ of the amide $C-C(O)$ group is the same as alkanes, 10 aldehydes, carboxylic acids, and carboxylic acid esters, -1.85836 eV , where both energy contributions are given by Eq. (14.513). Also, as in the case of aldehydes, $C_{1o} = 2C_1$ in Eq. (15.52).

In order to match energy throughout the chain of the amide molecule, $E_T(atom - atom, msp^3.AO)$ of the $C-N$ -bond MO in Eq. (15.52) due to the charge donation 15 from the C and N atoms to the MO is -1.65376 eV . It is based on the energy match between the $C2sp^3$ HO of the carbonyl and the primary amino group NH_2 . It is given by the linear combination of -0.92918 eV (Eq. (14.513)) which matches the contiguous $C-C(O)$ or $HC(O)$ group and -0.72457 eV (Eq. (14.151)), the contribution of a primary amino group given in the Primary Amines section.

20 The symbols of the functional groups of alkyl amides are given in Table 15.111. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl amides are given in Tables 15.112, 15.113, and 15.114, respectively. The total energy of each alkyl amide given in Table 15.115 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.114 corresponding 25 to functional-group composition of the molecule. The bond angle parameters of alkyl amides determined using Eqs. (15.79-15.108) are given in Table 15.116.

Table 15.111. The symbols of functional groups of alkyl amides.

Functional Group	Group Symbol
CH (formamide) group	$C-H$ (i)
C-C(O)	$C-C(O)$
C=O (formamide)	$C=O$ (i)
C=O (alkyl amide)	$C=O$ (ii)
(O)C-N (formamide)	$C-N$ (i)
(O)C-N (alkyl amide)	$C-N$ (ii)
NH ₂ group	NH ₂
CH ₃ group	$C-H$ (CH ₃)
CH ₂ group	$C-H$ (CH ₂)
CH (alkyl) group	$C-H$ (ii)
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.112. The geometrical bond parameters of alkyl amides and experimental values [1].

Parameter	C-H (i)	C=O (i)	C-N (i)	NH ₂	C-H (CH ₃)	C-H (CH ₃)	C-H (CH ₃)	C-H (ii)	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)
σ (°)	1.67465	1.200799	1.29907	1.32297	1.64920	1.67122	1.67465	2.12499	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
σ' (°)	1.05661	1.12613	1.1977	0.97065	1.04856	1.05553	1.05661	1.45744	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length 2c' (Å)	1.11827	1.20243	1.20628	1.02729	1.10974	1.11713	1.11827	1.54280	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.125 (formamide)	1.212 (formamide)	1.220 (acetamide) 1.225 (N-methylacetamide)	1.027 (formamide) 1.022 (acetamide)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
μ_c (e)	1.29924	0.61267	0.62331	0.89894	1.27295	1.29369	1.29924	1.54616	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
σ	0.63093	0.88018	0.87737	0.73369	0.63380	0.63159	0.63093	0.68600	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.114. The energy parameters (eV) of functional groups of alkyl amides.

Parameters	C-H (i)	C=O (i)	C-N (i)	C-N (ii)	NH ₂	CH ₃	CH ₂	C-H (ii)	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)
Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
η_1	1	2	1	1	2	3	2	1	1	1	1	1	1	1
η_2	0	0	0	0	0	2	1	0	0	0	0	0	0	0
η_3	0	0	0	0	1	0	0	0	0	0	0	0	0	0
ζ_1	0.75	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
ζ_2	1	1	1	1	0.9613	1	1	1	1	1	1	1	1	1
ζ_3	1	1	1	1	0.75	1	1	1	1	1	1	1	1	1
ζ_4	0.91771	0.85395	0.91140	0.91140	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
ζ_5	0	2	0	0	0	0	1	1	0	0	0	1	1	0
ζ_6	1	2	4	2	1	1	1	1	2	2	2	2	2	2
ζ_7	0	0	0	0	2	3	2	1	0	0	0	0	0	0
ζ_8	0.75	1	0.5	0.5	1.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
ζ_9	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{10}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{11}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{12}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{13}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{14}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{15}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{16}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{17}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{18}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{19}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{20}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{21}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{22}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{23}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{24}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{25}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{26}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{27}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{28}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{29}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{30}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{31}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{32}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{33}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{34}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{35}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{36}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{37}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{38}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{39}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{40}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{41}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{42}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{43}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{44}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{45}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{46}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{47}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{48}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{49}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{50}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{51}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{52}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{53}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{54}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{55}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{56}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{57}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{58}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{59}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{60}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{61}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{62}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{63}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{64}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{65}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{66}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{67}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{68}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{69}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{70}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{71}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{72}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{73}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{74}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{75}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{76}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{77}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{78}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{79}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{80}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{81}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{82}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{83}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{84}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{85}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{86}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{87}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{88}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{89}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{90}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{91}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{92}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{93}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{94}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{95}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{96}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{97}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{98}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{99}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{100}	1	1	1	1	1	1	1	1	1	1	1	1	1	1

Table 15.115. The total bond energies of alkyl amides calculated using the functional group composition and the energies of Table 15.114 compared to the experimental values [3].

Table 1. Bond energies of 1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37,38,39,40,41,42,43,44,45,46,47,48,49,50,51,52,53,54,55,56,57,58,59,60,61,62,63,64,65,66,67,68,69,70,71,72,73,74,75,76,77,78,79,80,81,82,83,84,85,86,87,88,89,90,91,92,93,94,95,96,97,98,99,100,101,102,103,104,105,106,107,108,109,110,111,112,113,114,115,116,117,118,119,120,121,122,123,124,125,126,127,128,129,130,131,132,133,134,135,136,137,138,139,140,141,142,143,144,145,146,147,148,149,150,151,152,153,154,155,156,157,158,159,160,161,162,163,164,165,166,167,168,169,170,171,172,173,174,175,176,177,178,179,180,181,182,183,184,185,186,187,188,189,190,191,192,193,194,195,196,197,198,199,200,201,202,203,204,205,206,207,208,209,210,211,212,213,214,215,216,217,218,219,220,221,222,223,224,225,226,227,228,229,230,231,232,233,234,235,236,237,238,239,240,241,242,243,244,245,246,247,248,249,250,251,252,253,254,255,256,257,258,259,260,261,262,263,264,265,266,267,268,269,270,271,272,273,274,275,276,277,278,279,280,281,282,283,284,285,286,287,288,289,290,291,292,293,294,295,296,297,298,299,300,301,302,303,304,305,306,307,308,309,310,311,312,313,314,315,316,317,318,319,320,321,322,323,324,325,326,327,328,329,330,331,332,333,334,335,336,337,338,339,340,341,342,343,344,345,346,347,348,349,350,351,352,353,354,355,356,357,358,359,360,361,362,363,364,365,366,367,368,369,370,371,372,373,374,375,376,377,378,379,380,381,382,383,384,385,386,387,388,389,390,391,392,393,394,395,396,397,398,399,400,401,402,403,404,405,406,407,408,409,410,411,412,413,414,415,416,417,418,419,420,421,422,423,424,425,426,427,428,429,430,431,432,433,434,435,436,437,438,439,440,441,442,443,444,445,446,447,448,449,450,451,452,453,454,455,456,457,458,459,460,461,462,463,464,465,466,467,468,469,470,471,472,473,474,475,476,477,478,479,480,481,482,483,484,485,486,487,488,489,490,491,492,493,494,495,496,497,498,499,500,501,502,503,504,505,506,507,508,509,510,511,512,513,514,515,516,517,518,519,520,521,522,523,524,525,526,527,528,529,530,531,532,533,534,535,536,537,538,539,540,541,542,543,544,545,546,547,548,549,550,551,552,553,554,555,556,557,558,559,560,561,562,563,564,565,566,567,568,569,570,571,572,573,574,575,576,577,578,579,580,581,582,583,584,585,586,587,588,589,590,591,592,593,594,595,596,597,598,599,600,601,602,603,604,605,606,607,608,609,610,611,612,613,614,615,616,617,618,619,620,621,622,623,624,625,626,627,628,629,630,631,632,633,634,635,636,637,638,639,640,641,642,643,644,645,646,647,648,649,650,651,652,653,654,655,656,657,658,659,660,661,662,663,664,665,666,667,668,669,670,671,672,673,674,675,676,677,678,679,680,681,682,683,684,685,686,687,688,689,690,691,692,693,694,695,696,697,698,699,700,701,702,703,704,705,706,707,708,709,710,711,712,713,714,715,716,717,718,719,720,721,722,723,724,725,726,727,728,729,730,731,732,733,734,735,736,737,738,739,740,741,742,743,744,745,746,747,748,749,750,751,752,753,754,755,756,757,758,759,760,761,762,763,764,765,766,767,768,769,770,771,772,773,774,775,776,777,778,779,780,781,782,783,784,785,786,787,788,789,790,791,792,793,794,795,796,797,798,799,800,801,802,803,804,805,806,807,808,809,810,811,812,813,814,815,816,817,818,819,820,821,822,823,824,825,826,827,828,829,830,831,832,833,834,835,836,837,838,839,840,841,842,843,844,845,846,847,848,849,850,851,852,853,854,855,856,857,858,859,860,861,862,863,864,865,866,867,868,869,870,871,872,873,874,875,876,877,878,879,880,881,882,883,884,885,886,887,888,889,890,891,892,893,894,895,896,897,898,899,900,901,902,903,904,905,906,907,908,909,910,911,912,913,914,915,916,917,918,919,920,921,922,923,924,925,926,927,928,929,930,931,932,933,934,935,936,937,938,939,940,941,942,943,944,945,946,947,948,949,950,951,952,953,954,955,956,957,958,959,960,961,962,963,964,965,966,967,968,969,970,971,972,973,974,975,976,977,978,979,980,981,982,983,984,985,986,987,988,989,990,991,992,993,994,995,996,997,998,999,1000,1001,1002,1003,1004,1005,1006,1007,1008,1009,1010,1011,1012,1013,1014,1015,1016,1017,1018,1019,1020,1021,1022,1023,1024,1025,1026,1027,1028,1029,1030,1031,1032,1033,1034,1035,1036,1037,1038,1039,1040,1041,1042,1043,1044,1045,1046,1047,1048,1049,1050,1051,1052,1053,1054,1055,1056,1057,1058,1059,1060,1061,1062,1063,1064,1065,1066,1067,1068,1069,1070,1071,1072,1073,1074,1075,1076,1077,1078,1079,1080,1081,1082,1083,1084,1085,1086,1087,1088,1089,1090,1091,1092,1093,1094,1095,1096,1097,1098,1099,1100,1101,1102,1103,1104,1105,1106,1107,1108,1109,1110,1111,1112,1113,1114,1115,1116,1117,1118,1119,1120,1121,1122,1123,1124,1125,1126,1127,1128,1129,1130,1131,1132,1133,1134,1135,1136,1137,1138,1139,1140,1141,1142,1143,1144,1145,1146,1147,1148,1149,1150,1151,1152,1153,1154,1155,1156,1157,1158,1159,1160,1161,1162,1163,1164,1165,1166,1167,1168,1169,1170,1171,1172,1173,1174,1175,1176,1177,1178,1179,1180,1181,1182,1183,1184,1185,1186,1187,1188,1189,1190,1191,1192,1193,1194,1195,1196,1197,1198,1199,1200,1201,1202,1203,1204,1205,1206,1207,1208,1209,1210,1211,1212,1213,1214,1215,1216,1217,1218,1219,1220,1221,12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N-ALKYL AND N,N-DIALKYL-AMIDES ($C_nH_{2n+1}NO$, $n = 2, 3, 4, 5 \dots \infty$)

The N-alkyl and N,N-dialkyl amides, $C_nH_{2n+1}NO$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. Formamide has a $HC=O$ moiety that comprises a more stable $C=O$ functional group and a CH functional group that is equivalent to that of the iso- CH group of branched-chain-alkyl portion of the N-alkyl or N,N-dialkyl amide. All amides further comprise a $C-N(R_1)R_2$ moiety that comprises two types of $C-N$ functional groups, one for formamide and the other for alkyl amides ($RC(O)N(R_1)R_2$ where R is alkyl). The N or N,N-dialkyl moiety comprises three additional groups depending on the alkyl substitution of the nitrogen. In the case of a single methyl or alkyl substitution, the $NH-C$ bond and NH are functional groups, and the $N-C$ bond of a di-substituted nitrogen is the third.

The alkyl portion of the N-alkyl or N,N-dialkyl amide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in N-alkyl or N,N-dialkyl amides are equivalent to those in branched-chain alkanes.

The NH functional group was solved in the Hydrogen Nitride (NH) section except that the energy of the $N-H$ MO is matched to the nitrogen-atom contribution to $\Delta E_{H,MO}(AO/HO)$ and $E_r(atom-atom,msp^3,AO)$ of the $C-N$ group. The $C-C(O)$ group, both N-alkyl or N,N-dialkyl amide $C=O$ groups, and both $C-N$ groups are equivalent to those given in the Amides section.

As in the case of primary amines, each $N-C$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the

$N-C$ H_2 -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.52) for the $N-C$ -bond MO given by Eq. (15.114) is $c_2(C2sp^3HO \text{ to } N) = 0.91140$.

$E_r(atom - atom, msp^3.AO)$ of the N-substituted amide $C-C(O)$ group is the same as alkanes, aldehydes, carboxylic acids, carboxylic acid esters, and amides, -1.85836 eV , where
 5 both energy contributions are given by Eq. (14.513). Also, as in the case of aldehydes, $C_{1o} = 2C_1$ in Eq. (15.52).

$E_r(atom - atom, msp^3.AO)$ (Eq. (15.52)) of the $C=O$ group of N-substituted alky amides and the $C=O$ group of N-substituted formamide are equivalent to those of the corresponding carboxylic acids, carboxylic esters, and amides. The values given in the
 10 Carboxylic Acids section are -2.69893 eV and -3.58557 eV , respectively.

$E_r(atom - atom, msp^3.AO)$ of both $C-N$ functional groups are the same as those of the corresponding groups of amides, -1.65376 eV . $E_r(atom - atom, msp^3.AO)$ of the singly-substituted $NH-C$ -bond MO in Eq. (15.52) due to the charge donation from the N and C atoms to the MO is -0.92918 eV . It is equivalent to that of tertiary amines and matches the
 15 energy of the $NH-C$ group to that of the $C-N$ group wherein $E_r(atom - atom, msp^3.AO)$ of the latter is a linear combination of -0.92918 eV (Eq. (14.513)) and -0.72457 eV (Eq. (14.151)). $E_r(atom - atom, msp^3.AO)$ of the doubly-substituted $N-C$ -bond MO is -0.72457 eV . It is equivalent to that of the contribution of each atom of a primary amine and also matches the energy of the $N-C$ group to that of the $C-N$ group by matching one of the
 20 components of $E_r(atom - atom, msp^3.AO)$ of the latter.

The symbols of the functional groups of N-alkyl and N,N-dialkyl amides are given in Table 15.117. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of N-alkyl and N,N-dialkyl amides are given in Tables 15.118, 15.119, and 15.120, respectively. The total energy of each N-alkyl
 25 or N,N-dialkyl amide given in Table 15.121 was calculated as the sum over the integer multiple of each $E_p(group)$ of Table 15.120 corresponding to functional-group composition of the molecule. The bond angle parameters of N-alkyl and N,N-dialkyl amides determined using Eqs. (15.79-15.108) are given in Table 15.122.

Table 15.117. The symbols of functional groups of N-alkyl and N,N-dialkyl amides.

Functional Group	Group Symbol
C-C(O)	$C - C(O)$
C=O (N-alkyl and N,N-dialkyl formamide)	$C = O$ (i)
C=O (N-alkyl and N,N-dialkyl amide)	$C = O$ (ii)
(O)C-N (N-alkyl and N,N-dialkyl formamide)	$C - N$ (i)
(O)C-N (N-alkyl and N,N-dialkyl amide)	$C - N$ (ii)
NH group	NH
N-C (N-alkyl)	$N - C$ (i)
N-C (N,N,-dialkyl)	$N - C$ (ii)
CH ₃ group	$C - H$ (CH_3)
CH ₂ group	$C - H$ (CH_2)
CH (alkyl) group	$C - H$
CC bond (n-C)	$C - C$ (a)
CC bond (iso-C)	$C - C$ (b)
CC bond (tert-C)	$C - C$ (c)
CC (iso to iso-C)	$C - C$ (d)
CC (t to t-C)	$C - C$ (e)
CC (t to iso-C)	$C - C$ (f)

Table 15.118. The geometrical bond parameters of N-alkyl and N,N-dialkyl amides and experimental values [1].

Parameter	C=O (i)	C=O (ii)	C-N (i)	C-N (ii)	NH	N-C (i)	N-C (ii)	C-H (CH ₃)	C-H (CH ₂)	C-H Group	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)
σ (Å)	1.207199	1.29907	1.70920	1.75370	1.28620	1.90313	1.97794	1.64920	1.67122	1.67465	2.17499	2.12499	2.10725	2.12499	2.10725	2.10725
ν (cm ⁻¹)	1.13613	1.13977	1.20716	1.24437	0.95706	1.40112	1.40609	1.04356	1.05553	1.05461	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length 2c' (Å)	1.20243	1.20628	1.33165	1.40135	1.01291	1.48288	1.48846	1.10074	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.520 (N-methylacetamide)	1.225 (N-methylacetamide)	1.368 (formamide)	1.380 (acetamide)		1.469 (N-methylacetamide)		1.107 (C-H propane)	1.107 (C-H propane)	1.122 (isobutane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.531 (butane)	1.532 (propane)
k_e (e ⁻)	1.64439	0.62331	1.10098	1.14968	0.85927	1.37505	1.30079	1.27825	1.29559	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
r	0.60887	0.88018	0.76490	0.75513	0.74410	0.71372	0.71104	0.63590	0.63159	0.63095	0.68600	0.68600	0.68818	0.68600	0.68818	0.68818

Table 15.119. The MO to HO intercept geometrical bond parameters of N-alkyl and N,N-dialkyl amides. R, R', R'' are H, methyl, or alkyl groups. E_p is $E_p(\text{vacuum} - \text{atom} - \text{group} - \text{AO})$.

Bond	Atom	E_p (eV) Bond 1	E_p (eV) Bond 2	E_p (eV) Bond 3	E_p (eV) Bond 4	Final Total Energy (eV)	r_{calc} (Å)	r_{exp} (Å)	$E_p(\text{vac})$ Final	$E_p(\text{vac})$ Final	θ (°)	θ_1 (°)	θ_2 (°)	d_1 (Å)	d_2 (Å)
$R'C_1(O)N(C_2H_5)-H$ (C=O (i) and (ii)) (C-N (i) and (ii))	N	-0.40368	-0.46459	0	0		0.02064	0.16418	-16.11722		113.47	64.53	62.49	0.59403	0.36303
$R'C_1(O)N(H)-C_2H_5$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (ii))	N	-0.40368	-0.46459	0	0		0.02064	0.16418	-16.11722		78.61	101.39	37.00	1.50779	0.16667
$R'C_1(O)N(H)-C_2H_5$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (ii))	C	-0.46459	0	0	0	-151.00028	0.01771	0.02913	-15.20914	-15.09918	83.37	96.63	40.00	1.50383	0.10371
$R'C_1(O)N(H)-C_2H_5C_2H_5R$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (ii))	N	-0.40368	-0.46459	0	0		0.02064	0.16418	-16.11722		78.61	101.39	37.00	1.50779	0.16667
$R'C_1(O)N(H)-C_2H_5C_2H_5R$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (ii))	C	-0.46459	-0.49218	0	0	-151.00946	0.01771	0.03185	-16.11952	-16.02666	78.02	101.39	36.64	1.57523	0.17413
$R'C_1(O)N(C_2H_5)-C_2H_5$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (ii))	N	-0.40368	-0.46459	-0.36229	0		0.03064	0.03078	-16.37720		75.57	104.43	35.35	1.61326	0.20697
$R'C_1(O)N(C_2H_5)-C_2H_5$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (ii))	C	-0.46459	0	0	0	-151.07708	0.01771	0.03982	-15.18204	-14.90717	82.59	97.41	39.70	1.51188	0.11549
$R'C_1(O)N(C_2H_5C_2H_5R)-C_2H_5$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (ii))	N	-0.40368	-0.46459	-0.36229	0		0.03064	0.03078	-16.37720		75.57	104.43	35.35	1.61326	0.20697
$R'C_1(O)N(C_2H_5C_2H_5R)-C_2H_5$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (ii))	C	-0.46459	0	0	0	-151.07708	0.01771	0.03982	-15.18204	-14.90717	82.59	97.41	39.70	1.51188	0.11549
$R'C_1(O)N(R')-C_2H_5C_2H_5R$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (ii))	N	-0.40368	-0.46459	-0.36229	0		0.03064	0.03078	-16.37720		75.57	104.43	35.35	1.61326	0.20697
$R'C_1(O)N(R')-C_2H_5C_2H_5R$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (ii))	C	-0.46459	-0.49218	0	0	-152.90716	0.01771	0.04418	-16.11722	-16.02636	77.13	103.88	36.38	1.59451	0.18612
$R'C_1(O)N(H)R$ (C=O (i)) (C-N (i)) (N-C (i)) <i>R = methyl or alkyl</i>	N	-0.40368	-0.46459	0	0		0.02064	0.04418	-16.11722		103.07	77.93	48.57	1.13090	0.19647
$R'C_1(O)N(H)R$ (C=O (i)) (C-N (i)) (N-C (i)) <i>R = methyl or alkyl</i>	C	-0.46459	-1.79278	0	0	-154.33515	0.01771	0.77991	-17.44541	-17.34555	96.81	83.19	44.70	1.21492	0.09244
$R'C_1(O)N(R')R$ (C=O (i)) (C-N (i)) (N-C (i)) <i>R, R' = methyl or alkyl</i>	N	-0.40368	-0.46459	-0.36229	0		0.03064	0.03078	-16.37720		101.03	78.97	47.79	1.14642	0.15855
$R'C_1(O)N(R')R$ (C=O (i)) (C-N (i)) (N-C (i)) <i>R, R' = methyl or alkyl</i>	C	-0.46459	-1.79278	0	0	-154.33515	0.01771	0.77991	-17.44541	-17.34555	96.81	83.19	44.70	1.21492	0.09244

$R, R' = \text{united or alkyl}$ $RH_2C_2C_2(O) - N(R)R$ (C=O (6)) (N-C (6)) (N-C (6))	N	-113268	-1.66159	0	0	-154.72121	0.91084	0.84418	-16.17722		98.16	81.84	46.52	1.30446	0.11892
$R = \text{united or alkyl}$ $RH_2C_2C_2(O) - N(R)H$ (C=O (6)) (C-N (6)) (N-C (6))	C_2	-0.93086	-1.31046	-0.02018	0	-154.72121	0.91071	0.75878	-17.53127	-17.74041	90.51	89.49	41.30	1.31155	0.00072
$R, R' = \text{united or alkyl}$ $RH_2C_2C_2(O) - N(R)R$ (C=O (6)) (C-N (6)) (N-C (6))	N	-0.83068	-0.30529	-0.30229	0		0.93084	0.81078	-16.37720		97.06	82.54	45.82	1.32220	0.10297
$R, R' = \text{united or alkyl}$ $RH_2C_2C_2(O) - N(R)R$ (C=O (6)) (C-N (6)) (N-C (6))	C_2	-0.93088	-1.31046	-0.02018	0	-154.72121	0.91071	0.75878	-17.53127	-17.74041	90.51	89.49	41.30	1.31155	0.00072
$R, R' = \text{united or alkyl}$ $RH_2C_2C_2(O) - N(R)R$ (C=O (6)) (C-N (6)) (N-C (6))	O	-1.79278	0	0	0		1.79278	0.81871	-16.61853		137.10	42.90	65.45	0.51035	0.59874
$R, R' = \text{united or alkyl}$ $RH_2C_2C_2(O) - N(R)R$ (C=O (6)) (C-N (6)) (N-C (6))	C_2	-1.72378	-0.82686	0	0	-154.72121	0.91071	0.75878	-17.53127	-17.74041	133.07	46.33	61.70	0.41582	0.33295
$R, R' = \text{united or alkyl}$ $RH_2C_2C_2(O) - N(R)R$ (C=O (6)) (C-N (6)) (N-C (6))	O	-1.31946	0	0	0		1.31946	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$R, R' = \text{united or alkyl}$ $RH_2C_2C_2(O) - N(R)R$ (C=O (6)) (C-N (6)) (N-C (6))	C_2	-1.72378	-0.82686	0	0	-154.72121	0.91071	0.75878	-17.53127	-17.74041	133.07	46.33	61.70	0.41582	0.33295
$R, R' = \text{united or alkyl}$ $RH_2C_2C_2(O) - N(R)R$ (C=O (6)) (C-N (6)) (N-C (6))	O	-1.72378	-0.82686	0	0	-154.72121	0.91071	0.75878	-17.53127	-17.74041	133.07	46.33	61.70	0.41582	0.33295
$R, R' = \text{united or alkyl}$ $RH_2C_2C_2(O) - N(R)R$ (C=O (6)) (C-N (6)) (N-C (6))	C_2	-1.72378	-0.82686	0	0	-154.72121	0.91071	0.75878	-17.53127	-17.74041	133.07	46.33	61.70	0.41582	0.33295
$R, R' = \text{united or alkyl}$ $RH_2C_2C_2(O) - N(R)R$ (C=O (6)) (C-N (6)) (N-C (6))	O	-1.72378	-0.82686	0	0	-154.72121	0.91071	0.75878	-17.53127	-17.74041	133.07	46.33	61.70	0.41582	0.33295
$R, R' = \text{united or alkyl}$ $RH_2C_2C_2(O) - N(R)R$ (C=O (6)) (C-N (6)) (N-C (6))	C_2	-1.72378	-0.82686	0	0	-154.72121	0.91071	0.75878	-17.53127	-17.74041	133.07	46.33	61.70	0.41582	0.33295
$R, R' = \text{united or alkyl}$ $RH_2C_2C_2(O) - N(R)R$ (C=O (6)) (C-N (6)) (N-C (6))	O	-1.72378	-0.82686	0	0	-154.72121	0.91071	0.75878	-17.53127	-17.74041	133.07	46.33	61.70	0.41582	0.33295
$R, R' = \text{united or alkyl}$ $RH_2C_2C_2(O) - N(R)R$ (C=O (6)) (C-N (6)) (N-C (6))	C_2	-1.72378	-0.82686	0	0	-154.72121	0.91071	0.75878	-17.53127	-17.74041	133.07	46.33	61.70	0.41582	0.33295
$R, R' = \text{united or alkyl}$ $RH_2C_2C_2(O) - N(R)R$ (C=O (6)) (C-N (6)) (N-C (6))	O	-1.72378	-0.82686	0	0	-154.72121	0.91071	0.75878	-17.53127	-17.74041	133.07	46.33	61.70	0.41582	0.33295
$R, R' = \text{united or alkyl}$ $RH_2C_2C_2(O) - N(R)R$ (C=O (6)) (C-N (6)) (N-C (6))	C_2	-1.72378	-0.82686	0	0	-154.72121	0.91071	0.75878	-17.53127	-17.74041	133.07	46.33	61.70	0.41582	0.33295

Table 15.120. The energy parameters (eV) of functional groups of N-alkyl and N,N-dialkyl amides

[illegible]

Table 15.121 The total bond energies of N-Halobenzonitriles calculated using the functional remain composition and the energies of Table 15.120 compared to the experimental values [37].

Table 15. [21]. The gas bond energies of N-alkyl and N-haloalkyl amides calculated using the functional group composition and the energies of Table 14, 120 compared to the experimental values [3]

Name	C-C (I)	C=C (I)	C≡C (I)	C-N (II)	NH	N-C (I)	N-C (II)	CH ₃	CH ₂	CH	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	Calculated Total Bond Energy (eV)	Experiment al Total Bond Energy (eV)	Relative Error
Formide	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	43.53142	47.594	0.00669
Gly-NH ₂	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	59.21404	59.890	-0.00341
NH ₂ -N-methylformamide	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	74.25849	74.390	-0.00355
NH ₂ -N-propylacetamide	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	84.39619	84.390	-0.00355

[illegible]

UREA (CH_4N_2O)

Urea, CH_4N_2O , comprises a $C=O$ functional group and two $C-NH_2$ moieties that each comprise a NH_2 functional group and a $C-N$ functional group. The $C=O$ group is equivalent to that given for formamide in the Amides section except that the energy terms due to oscillation in the transition state are matched to that of urea. The NH_2 and $C-N$ functional groups are also equivalent to those given in the Amides section. $E_r(atom-atom,msp^3.AO)$ (Eq. (15.52)) of the $C=O$ and $C-N$ groups are equivalent to those of formamide. The values given in the Amides section are -3.58557 eV , and -1.65376 eV , respectively.

The symbols of the functional groups of urea are given in Table 15.123. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of urea are given in Tables 15.124, 15.125, and 15.126, respectively. The total energy of urea given in Table 15.127 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.126 corresponding to functional-group composition of the molecule. The bond angle parameters of urea determined using Eqs. (15.79-15.108) are given in Table 15.128.

Table 15.123. The symbols of functional groups of urea.

Functional Group	Group Symbol
C=O (urea)	$C=O$
(O)C-N (urea)	$C-N$
NH_2 group	NH_2

Table 15.124. The geometrical bond parameters of urea and experimental values [1].

Parameter	C=O Group	C-N Group	NH ₂ Group
a (Å)	1.290799	1.70920	1.32197
c' (Å)	1.13613	1.30736	0.97065
Bond Length $2c'$ (Å)	1.20243	1.38365	1.02729
Exp. Bond Length (Å)	1.212 (formamide)	1.358 (formamide) 1.022 (acetamide)	1.027
a_{exp} (Å)	0.61267	1.10098	0.89894
c	0.88018	0.76490	0.73369

Table 15.125. The MO to HO intercept geometrical bond parameters of urea. E_r is $E_r(\text{atom} - \text{atom}, \text{exp}, \text{AO})$.

Bond	Atom	E_r (eV) Bond 1	E_r (eV) Bond 2	E_r (eV) Bond 3	E_r (eV) Bond 4	Final Total Energy C2sp ² (eV)	r_{bond} (Å)	r_{bond} (Å)	E_{C2sp^2} (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (Å)	d_2 (Å)
$H_1NCO(NH)-H$	N	-0.82588	0	0	0		0.93084	0.86923	-15.65263	113.90	66.10	62.13	0.41943	0.35222
$H_1NCO(NH)-NH_2$	N	-0.82588	0	0	0		0.93084	0.86923	-15.65263	103.93	78.07	50.02	1.09316	0.20922
$H_1NCO(NH)-NH_2$	C	-0.82588	-1.79278	-0.12688	0	-155.06323	0.91771	0.74461	-18.37229	91.56	80.64	42.45	1.26106	0.04630
$H_1NC_2(NH_2)=O$	O	-1.79278	0	0	0	1.00000	1.00000	0.81871	-16.61853	137.10	43.90	65.45	0.51633	0.38978
$H_1NC_2(NH_2)=O$	C	-1.79278	-0.82488	-0.12688	0	-155.06323	0.91771	0.74461	-18.37229	113.82	66.18	61.27	0.52034	0.51539

Table 15.126. The energy parameters (eV) of functional groups of urea.

Parameters	C = O Group	C - N Group	NH ₂ Group
n_1	2	1	2
n_2	0	0	0
n_3	0	0	1
C_1	0.5	0.5	0.75
C_2	1	1	0.93613
c_1	1	1	0.75
c_2	0.85395	0.91140	1
c_3	2	0	0
c_4	4	2	1
c_5	0	0	2
C_{10}	0.5	0.5	1.5
C_{20}	1	1	1
V_r (eV)	-112.61934	-38.24008	-78.77719
V_p (eV)	23.95107	10.40705	28.03446
T (eV)	43.62389	11.18655	29.77286
V_m (eV)	-21.81195	-5.59327	-14.88643
$E(\text{AO} \text{HO})$ (eV)	0	-14.63489	-14.53414
$\Delta E_{H_2\text{MO}}(\text{AO} \text{HO})$ (eV)	-3.58557	-5.23932	-1.65376
$E_r(\text{AO} \text{HO})$ (eV)	3.58557	-9.39557	-12.88038
$E(n, \text{AO} \text{HO})$ (eV)	0	0	-14.53414
$E_r(n, \text{MO})$ (eV)	-63.27075	-31.63533	-48.73668
$E_r(\text{atom} - \text{atom}, \text{msp}^3, \text{AO})$ (eV)	-3.58557	-1.65376	0
$E_r(\text{MO})$ (eV)	-66.85630	-33.28912	-48.73660
ω (10^{15} rad / s)	19.9334	13.0822	59.4067
E_K (eV)	13.12053	8.61093	39.10250
\bar{E}_D (eV)	-0.23955	-0.19325	-0.39136
\bar{E}_{Kvb} (eV)	0.21747 [32]	0.17358 [33]	0.40929 [22]
\bar{E}_{ex} (eV)	-0.13081	-0.10647	-0.18672
E_{mag} (eV)	0.11441	0.14803	0.14185
$E_r(\text{ring})$ (eV)	-67.11793	-33.39559	-49.11003
$E_{\text{total}}(r_1, \text{AO} \text{HO})$ (eV)	-14.63489	-14.63489	-14.53414
$E_{\text{total}}(r_2, \text{AO} \text{HO})$ (eV)	0	0	-13.59844
$E_U(\text{Group})$ (eV)	8.34955	4.12581	7.37901

Table 15.127. The total bond energies of urea calculated using the functional group composition and the energies of Table 15.126 compared to the experimental values [3].

Formula	Name	C = O Group	C - N Group	NH ₂ Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH ₄ N ₂ O	Urea	1	2	2	31.35919	31.393	0.00108

CARBOXYLIC ACID HALIDES ($C_nH_{2n-1}OX$, $X = F, Cl, Br, I$; $n = 1, 2, 3, 4, 5 \dots \infty$)

The alkyl carboxylic acid halides, $C_nH_{2n-1}OX$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. All carboxylic acid halides further comprise a $C-X$ functional group where X is a halogen atom. The alkyl portion of the alkyl carboxylic acid halide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acids are equivalent to those in branched-chain alkanes.

The alkyl carboxylic acid halide $C=O$ and $C-C(O)$ groups are equivalent to those given in the Aldehydes section and the Ketones section, respectively. The values of $E_r(atom-atom,msp^3.AO)$ given in these sections are -2.69893 eV and -1.44915 eV , respectively.

As in the case of alkyl halides, each $(O)C-X$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the X AO to form a MO permits each participating orbital to decrease in radius and energy. For example, to meet the equipotential condition of the union of the $(O)C-Cl$ H_2 -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor C_2 of Eq. (15.52) for the $(O)C-Cl$ -bond MO given by Eq. (15.111) is $C_2(C2sp^3HO\text{ to }Cl) = 0.81317$. The solution is equivalent to that of the alkyl chloride bond except that the energy parameters corresponding to oscillation in the transition state are matched to those of a carboxylic acid chloride.

As in the case with the $C-Cl$ group of alkyl chlorides, $E_r(atom-atom,msp^3.AO)$ of the $(O)C-Cl$ -bond MO in Eq. (15.52) of alkyl carboxylic acid chlorides due to the charge donation from the C and Cl atoms to the MO is -1.44915 eV where both energy contributions

are given by Eq. (14.511). This matches the energy of the $C - C(O)$ functional group with that of the $(O)C - Cl$ group within the carboxylic acid chloride molecule.

The symbols of the functional groups of alkyl carboxylic acid chlorides are given in Table 15.129. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)),
5 and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid chlorides are given in Tables 15.130, 15.131, and 15.132, respectively. The total energy of each alkyl carboxylic acid chloride given in Table 15.133 was calculated as the sum over the integer multiple of each $E_n(\text{Group})$ of Table 15.132 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl carboxylic acid chlorides determined using Eqs.
10 (15.79-15.108) are given in Table 15.134.

Table 15.129. The symbols of functional groups of alkyl carboxylic acid chlorides.

Functional Group	Group Symbol
C-C(O)	C=O
C=O	C-Cl
C-O (alkyl carboxylic acid chloride)	C-H (CH ₁)
(O)C-Cl	C-H (CH ₂)
CH ₃ group	C-H
CH ₂ group	C-H
CH (alkyl) group	C-H
CC bond (n-C)	C-H
CC bond (iso-C)	C-H
CC bond (tert-C)	C-H
CC (iso to iso-C)	C-H
CC (1 to 1-C)	C-H
CC (1 to iso-C)	C-H

Table 15.130. The isomeric bond parameters of alkyl carboxylic acid chlorides and experimental values [1].

Parameter	C-C(O) Group	C=O Group	C-Cl Group	C-H (CH ₁) Group	C-H (CH ₂) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
α (°)	2.04740	1.39007	2.32621	1.64920	1.67123	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
α' (°)	1.43087	1.13977	1.69136	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length	1.51437	1.20628	1.79005	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
$2\alpha'$ (°)	1.520 (acetone)	1.187 (acetyl chloride)	1.798 (acetyl chloride)	1.107 (C-H propane)	1.107 (C-H propane)	1.122 (isobutane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)
Exp. Bond Length (Å)	1.518 (2-butanone)	1.214 (acetic acid)	1.59705	1.117 (C-H butane)	1.117 (C-H butane)	1.29924	1.531 (butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)
α, α' (°)	1.46439	0.62331	1.59705	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
α	0.69887	0.87737	0.77709	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.131. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid chlorides. R, R', R'' are H or alkyl groups. E_f is $E_f(atom - atom, mpy^2, AO)$.

Bond	Atom	E_f (eV) Bond 1	E_f (eV) Bond 2	E_f (eV) Bond 3	E_f (eV) Bond 4	Final Total Energy C2sp ² (eV)	r_{final} (a_0)	r_{final} (a_0)	$E_{calculated}$ (eV) Final	$E(C2sp^2)$ (eV) Final	θ' ($^\circ$)	θ_1 ($^\circ$)	θ_2 ($^\circ$)	d_1 (a_0)	d_2 (a_0)
$H_2C_2C(O)-Cl$	Cl	-0.72457	0	0	0	-154.1430	0.91771	0.87495	-15.55033	-17.43350	59.62	110.38	30.90	1.99599	0.30463
$H_2C_2C(O)-Cl$	C ₁	-1.34946	-0.72457	-0.72457	0	-154.1430	0.91771	0.77199	-17.60016	-17.43350	54.69	125.31	23.23	2.13760	0.44625
$H_2C_2C(O)=O$	O	-1.34946	0	0	0	-154.1430	1.00000	0.84115	-16.17521	-17.43350	137.27	42.73	66.31	0.52153	0.51784
$H_2C_2C(O)=O$	C ₁	-1.34946	-0.72457	-0.72457	0	-154.1430	0.91771	0.77199	-17.62036	-17.43350	134.28	45.72	62.45	0.60076	0.33901
$H_2C_2C(O)-Cl$	C ₂	-0.72457	-1.34946	-0.72457	0	-154.1430	0.91771	0.77199	-17.62036	-17.43350	59.30	120.70	26.96	1.82495	0.39408
$H_2C_2C(O)-Cl$	C ₃	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	73.62	106.38	34.96	1.67762	0.24675
$C-H(CH_3)$	C	-0.92918	0	0	0	-152.34487	0.91771	0.86359	-15.75493	-15.36407	77.49	102.51	41.48	1.23564	0.18708
$C-H(CH_3)$	C	-0.92918	-0.92918	0	0	-153.74066	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H(CH)(H)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77347	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_2C_2C(H)CH_2-$ (C-C(a))	C ₁	-0.92918	0	0	0	-152.34487	0.91771	0.86359	-15.75493	-15.36407	63.82	116.18	30.08	1.83579	0.38106
$H_2C_2C(H)CH_2-$ (C-C(b))	C ₂	-0.92918	-0.92918	0	0	-153.74066	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_2C(H_2C_2-R)HCH_2-$ (C-C(a))	C ₁	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77347	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_2C(H_2C_2-R)HCH_2-$ (C-C(b))	C ₂	-0.92918	-0.72457	-0.72457	-0.72457	-154.18600	0.91771	0.75889	-17.92866	-17.73779	48.31	131.79	21.74	1.92734	0.50570
$R-H_2C_2C(H_2C_2-R)HCH_2-$ (C-C(c))	C ₃	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77347	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_2C(H_2C_2-R)HCH_2-$ (C-C(d))	C ₄	-0.72457	-0.72457	-0.72457	-0.72457	-154.41399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$R-H_2C_2C(H_2C_2-R)HCH_2-$ (C-C(e))	C ₅	-0.72457	-0.92918	-0.92918	0	-154.19663	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$R-H_2C_2C(H_2C_2-R)HCH_2-$ (C-C(f))	C ₆	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.132. The energy parameters (eV) of functional groups of alkyl carboxylic acid chlorides.

Parameters	C-C(O)	C=O	C-Cl	CH ₃	CH ₂	C-H (H)	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)
η_1	1	2	1	3	2	1	1	1	1	1	1	1
η_2	0	0	0	2	1	0	0	0	0	0	0	0
η_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	0.81317	1	1	1	1	1	1	1	1	1
C_3	1	1	1	1	1	1	1	1	1	1	1	1
C_4	0.91771	0.85395	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
C_5	0	2	1	0	1	1	0	0	0	1	1	0
C_6	2	4	2	1	1	1	2	2	2	2	2	2
C_7	0	0	0	3	2	1	0	0	0	0	0	0
C_8	1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_9	1	1	0.81317	1	1	1	1	1	1	1	1	1
V_1 (eV)	-30.19634	-111.25473	-29.68411	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_2 (eV)	9.50874	23.87467	8.04432	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	7.37432	42.82081	6.38036	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_3 (eV)	-3.68716	-21.41040	-3.19018	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.43250	-3.38732	-3.43250	-3.43250
$E_{\text{bond}}(eV)$	-14.63489	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{\text{HOMO}}(eV)$	0	-2.69893	-1.44915	0	0	0	0	0	0	0	0	0
$E_g(eV)$	-14.63489	2.69893	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_{\text{HOMO}}(eV)$	-31.63534	-63.77074	-31.63536	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_{\text{LUMO}}(eV)$	-1.44915	-2.69893	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_{\text{HOMO}}(eV)$	-33.08452	-65.96966	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega(10^3 \text{ cm}^{-1})$	16.4962	59.4034	7.42995	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	15.4846	9.55643
$E_{\text{HOMO}}(eV)$	10.85807	39.10034	4.89052	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	10.19220	6.29021
$E_{\text{LUMO}}(eV)$	-0.21568	-0.40804	-0.14475	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{\text{HOMO}}(eV)$	0.14655	0.21077	0.09063	0.35532	0.35532	0.35532	0.12312	0.12312	0.09844	0.12312	0.12312	0.12312
$E_{\text{LUMO}}(eV)$	-0.14240	-0.30266	-0.09943	-0.27757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{\text{HOMO}}(eV)$	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\text{LUMO}}(eV)$	-33.22692	-66.57498	-33.18395	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.24376	-33.59732	-33.18712	-33.18712
$E_{\text{HOMO}}(eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{\text{LUMO}}(eV)$	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{\text{HOMO}}(eV)$	3.95714	7.80660	3.76614	12.49186	7.83016	3.76601	4.37754	4.29921	3.97398	4.17951	3.62128	3.91724

Table 15.133. The total bond energies of alkyl carboxylic acid chlorides calculated using the functional group composition and the energies of Table 15.102 compared to the experimental values [31].

Formula	Name	C-C(O)	C=O	C-Cl	CH ₃	CH ₂	CH	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C-H-ClO	Acetyl chloride	1	1	1	1	0	0	0	0	0	0	0	0	27.02174	27.090	-0.06815

CARBOXYLIC ACID ANHYDRIDES ($C_nH_{2n-2}O_3$, $n = 2, 3, 4, 5 \dots \infty$)

The alkyl carboxylic acid anhydrides, $C_nH_{2n-2}O_3$, have two $(O)C-O$ moieties that each comprise $C=O$ and $C-O$ functional groups. The single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. The alkyl portion of the alkyl carboxylic acid anhydride may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n -alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t -butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t -butyl, and t -butyl to t -butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acid anhydrides are equivalent to those in branched-chain alkanes.

The alkyl carboxylic acid anhydride $C=O$ and $C-C(O)$ groups are equivalent to those given in the Carboxylic Acid Esters section and the Ketones section, respectively. The values of $E_r(atom-atom,msp^3.AO)$ given in these sections are $-2.69893 eV$ and $-1.44915 eV$, respectively. The $C-O$ group is also equivalent to that given in the Carboxylic Acid Esters section except that $E_r(atom-atom,msp^3.AO)$ is equivalent to that of an alkyl ether as given in the corresponding section and the energy terms due to oscillation in the transition state are matched to that of a carboxylic acid anhydride.

For the $C-O$ group, $E_r(atom-atom,msp^3.AO)$ is $-1.65376 eV$. It is based on the energy match between the O AO and the $C2sp^3$ HO of each $C-C(O)$ group and is given by the linear combination of $-0.72457 eV$ (Eq. (14.151)) and $-0.92918 eV$ (Eq. (14.513)), respectively. This matches $-0.72457 eV$, the energy contribution of each of the $C2sp^3$ HOs to each $C-C(O)$ functional group, with that of the corresponding energy component of the $C-O$ group and gives a minimum energy within the carboxylic acid anhydride molecule.

The symbols of the functional groups of alkyl carboxylic acid anhydrides are given in Table 15.135. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid anhydrides are given in Tables 15.136, 15.137, and 15.138, respectively. The total energy of each alkyl

carboxylic acid anhydride given in Table 15.139 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.138 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl carboxylic acid anhydrides determined using Eqs. (15.79-15.108) are given in Table 15.140.

Table 15.135. The symbols of functional groups of alkyl carboxylic acid anhydrides

Functional Group	Group Symbol
C-C(O)	C-C(O)
C=O (alkyl carboxylic acid anhydrides)	C=O
(O)C=O	C=O
CH ₃ group	C-H (CH ₃)
CH ₂ group	C-H (CH ₂)
CH (alkyl) group	C-H
CC bond (n-C)	C-C' (a)
CC bond (iso-C)	C-C' (b)
CC bond (tert-C)	C-C' (c)
CC (iso to iso-C)	C-C' (d)
CC (1 to 1-C)	C-C' (e)
CC (1 to iso-C)	C-C' (f)

Table 15.136. The geometrical bond parameters of alkyl carboxylic acid anhydrides and experimental values [1].

Parameter	C-C(O) Group	C=O Group	C-O Group	C-H (CH ₃) Group	C-H (CH ₂) Group	C-H Group	C-C' (a) Group	C-C' (b) Group	C-C' (c) Group	C-C' (d) Group	C-C' (e) Group	C-C' (f) Group
σ (°)	2.04740	1.29907	1.73490	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
τ (°)	1.43087	1.13977	1.31716	1.04856	1.05353	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length 2r' (Å)	1.31437	1.20628	1.39402	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.520 (acetone)	1.214 (acetic acid)	1.393 (avg. methyl formate)	1.107 (C-H propane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
Δ (°)	1.46459	0.62331	1.12915	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
Δ (°)	0.69887	0.87137	0.75921	0.65580	0.65159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15: 137. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid anhydrides. R, R', R'' are H or alkyl groups. E_p is $E_p(\text{atom} - \text{atom}, \text{map}, \text{AO})$.

Bond	Atom	E_p (eV) Bond 1	E_p (eV) Bond 2	E_p (eV) Bond 3	E_p (eV) Bond 4	Final Total Energy C_{2sp^2} (eV)	r_{map} (a_0)	r_{map} (a_0)	E_{map} (eV) Final	$E(C_{2sp^2})$ (eV) Final	θ^* ($^\circ$)	θ_i ($^\circ$)	θ_o ($^\circ$)	d_i (a_0)	d_o (a_0)
$RC_2H_5C_2(O)-O-C_2(O)C_2H_5R'$	O_p	-0.82688	-0.82688	0	0	-154.51600	0.91771	0.82562	-16.47951	-17.33580	94.32	91.08	46.34	1.19766	0.11049
$RC_2H_5C_2(O)-O-C_2(O)C_2H_5R'$	C_p	-0.82688	-1.34946	-0.82688	0	-154.51600	0.91771	0.76753	-17.72667	-17.33580	93.21	85.79	42.74	1.23417	0.04393
$RC_2H_5C_2(O)-O-C_2(O)C_2H_5R'$	O_p	-1.34946	0	0	0	-154.51600	0.91771	0.84115	-16.17321	-17.33580	137.27	42.79	66.31	0.52193	0.61784
$RC_2H_5C_2(O)-O-C_2(O)C_2H_5R'$	C_p	-1.34946	-0.72437	-0.82688	0	-154.51600	0.91771	0.76753	-17.72667	-17.33580	134.04	45.92	62.20	0.60885	0.33394
$RC_2H_5C_2(O)-O-C_2(O)C_2H_5R'$	C_p	-0.72437	-1.34946	-0.82688	0	-154.51600	0.91771	0.76753	-17.72667	-17.33580	58.55	121.45	26.56	1.83133	0.40045
$H_2C_2-C_2(O)C_2H_5R'$	C_p	-0.72437	0	0	0	-153.34026	0.91771	0.87495	-15.53033	-15.35946	73.02	100.31	34.98	1.67762	0.34075
$RH_2C_2-C_2(O)C_2H_5R'$	C_p	-0.72437	-0.92018	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28865	67.40	112.60	31.36	1.74821	0.31734
$R=alkyl$	C'	-0.92018	0	0	0	-152.54487	0.91771	0.80339	-15.75403	-15.56407	77.49	102.51	41.48	1.23564	0.18703
$C'-H (CH_3)$	C'	-0.92018	-0.92018	0	0	-151.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35466	0.39933
$C'-H (CH_3)$	C'	-0.92018	-0.92018	0	0	-154.40324	0.91771	0.77247	-17.61330	-17.42344	61.10	118.39	31.37	1.62985	0.37206
$H_2C_2-C_2H_5CH_3$	C_p	-0.92018	0	0	0	-152.54487	0.91771	0.80339	-15.75403	-15.56407	63.82	116.18	30.08	1.83379	0.38106
$H_2C_2-C_2H_5CH_3$	C_p	-0.92018	-0.92018	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90390	0.45117
$R-H_2C_2(H_2C_2-R)HCH_3$	C_p	-0.92018	-0.92018	-0.92018	0	-154.40324	0.91771	0.77247	-17.61330	-17.42344	49.30	131.70	21.90	1.97162	0.51388
$R-H_2C_2(H_2C_2-R)HCH_3$	C_p	-0.92018	-0.72437	-0.72437	-0.72437	-154.11860	0.91771	0.51889	-17.97866	-17.73779	48.21	131.79	21.74	1.93734	0.50370
$tert-C_2(H_2C_2-R)HCH_3$	C_p	-0.92018	-0.92018	-0.92018	0	-154.40324	0.91771	0.77247	-17.61330	-17.42344	48.30	131.70	21.90	1.97162	0.51388
$tert-C_2(H_2C_2-R)HCH_3$	C_p	-0.72437	-0.72437	-0.72437	-0.72437	-154.51399	0.91771	0.76763	-17.93866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tert-C_2(H_2C_2-R)HCH_3$	C_p	-0.72437	-0.92018	-0.92018	0	-154.19865	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$tert-C_2(H_2C_2-R)HCH_3$	C_p	-0.72437	-0.72437	-0.72437	-0.72437	-154.51399	0.91771	0.76763	-17.93866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.138. The energy parameters (eV) of functional groups of alkyl carboxylic acid anhydrides.

Parameters	C-C(O)	C=O	C-O	C-H	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	C-C (g)
Δ_f	1	2	1	3	1	1	1	1	1	1	1
Δ_g	0	0	0	2	0	0	0	0	0	0	0
Δ_h	0	0	0	0	0	0	0	0	0	0	0
Δ_i	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5
Δ_j	1	1	1	1	1	1	1	1	1	1	1
Δ_k	1	1	1	1	1	1	1	1	1	1	1
Δ_l	0.91771	0.85395	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
Δ_m	0	2	0	0	0	0	0	0	0	0	0
Δ_n	2	4	2	1	2	2	2	2	2	2	2
Δ_o	0	0	0	3	0	0	0	0	0	0	0
Δ_p	1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5
Δ_q	1	1	1	1	1	1	1	1	1	1	1
Δ_r	-30.19634	-111.25473	-35.08488	-107.32728	-70.41425	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214
Δ_s	9.50874	23.87467	10.32958	38.92728	25.78002	9.33352	9.33352	9.33352	9.33352	9.33352	9.33352
Δ_t	7.37432	42.82081	10.11150	32.33914	21.06675	10.48582	6.77464	6.77464	6.77464	6.77464	6.77464
Δ_u	-5.63716	-21.41040	-5.03375	-10.26957	-10.53337	-3.24291	-3.24291	-3.24291	-3.24291	-3.24291	-3.24291
Δ_v	-14.63489	0	-14.63489	-15.56407	-15.56407	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Δ_w	0	-2.69893	-2.69893	0	0	0	0	0	0	0	0
Δ_x	-14.63489	2.69893	-11.93596	-15.56407	-15.56407	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Δ_y	-31.63334	-63.27074	-31.63341	-67.69451	-49.66493	-31.63337	-31.63337	-31.63337	-31.63337	-31.63337	-31.63337
Δ_z	-1.44915	-2.69893	-1.65376	0	0	0	0	0	0	0	0
Δ_{total}	-33.08452	-65.96866	-33.28912	-67.69450	-49.66493	-31.63337	-31.63337	-31.63337	-31.63337	-31.63337	-31.63337
ω	16.4962	59.4034	24.3037	24.9286	24.2751	24.1759	24.1759	24.1759	24.1759	24.1759	24.1759
$\Delta_{\text{C-C}}$	10.83807	39.10034	16.03660	16.40846	15.97831	15.91299	6.21159	6.21159	6.21159	6.21159	6.21159
$\Delta_{\text{C=O}}$	-0.21568	-0.48804	-0.26373	-0.25352	-0.25017	-0.24966	-0.16315	-0.20896	-0.16315	-0.16315	-0.16315
$\Delta_{\text{C-O}}$	0.14655	0.21077	0.15038	0.33532	0.34532	0.34532	0.12312	0.17978	0.09944	0.12312	0.12312
$\Delta_{\text{C-H}}$	-0.14240	-0.30266	-0.19554	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10260	-0.10260
$\Delta_{\text{C-C (a)}}$	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$\Delta_{\text{C-C (b)}}$	-33.22692	-66.57498	-33.48466	-67.92207	-49.80966	-31.70737	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732
$\Delta_{\text{C-C (c)}}$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$\Delta_{\text{C-C (d)}}$	0	0	0	-13.59844	-13.59844	0	0	0	0	0	0
$\Delta_{\text{C-C (e)}}$	3.95714	7.80660	4.21488	12.49186	7.83016	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.139. The total bond energies of alkyl carboxylic acid anhydrides calculated using the functional group composition and the energies of Table 15.138 compared to the experimental values [9].

Formula	Name	C-C(O)	C=O	C-O	C-H	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	Calculated Total Bond Energy (kJ/mol)	Experimental Total Bond Energy (kJ/mol)	Relative Error
$\text{CH}_3\text{CO}_2\text{CH}_3$	Acetic anhydride	2	2	2	2	0	0	0	0	0	0	56.84095	56.84095	0.00013
$\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$	Propionic anhydride	2	2	2	2	0	0	0	0	0	0	81.24516	81.401	0.00177

Table 15.140. The bond angle parameters of alkyl carboxylic acid anhydrides and experimental values [1]. In the calculation of θ_1 , the parameters from the preceding angle were used. E_p is $E_p(\text{atom} - \text{atom}, \text{angle}^\circ, \text{AO})$.

Atom of Angle	$2c_1$ Bond 1 (θ_1)	$2c_2$ Bond 2 (θ_2)	$2c_3$ Bond 3 (θ_3)	E_p Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	E_p Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	E_p Atom 3	Atom 3 Hybridization Designation (Table 15.3.A)	ζ_1	ζ_2	ζ_3	θ_1 ($^\circ$)	θ_2 ($^\circ$)	θ_3 ($^\circ$)	Cal. θ ($^\circ$)	Exp. θ ($^\circ$)
$\angle O_1 C_1 O_2$	2.37854	2.62431	4.3012	-16.17521 C_1	12	-16.47951 O_2	21	0.84115	0.82562	1	1	1	0.83239	-1.44015		122.00	121.7 [10] (acetic anhydride)
$\angle C_1 O_1 C_2$	2.62431	2.62431	4.4944	-17.30634 C_2	36	-17.30634 O_1	36	0.78617	0.78617	1	1	1	0.78617	-1.83836		117.09	115.8 [36] (acetic anhydride)
$\angle C_1 C_1 O_1$	2.36175	2.62431	4.4944	-15.55033 C_1	5	-13.61806 O_1	O	0.87495	0.83375	1	1	1	0.86445	-1.44915		109.65	108.3 [36] (acetic anhydride)
$\angle C_1 C_1 O_2$	2.36175	2.37854	4.6168	-16.47951 C_2	21	-15.61806 O_2	O	0.82562	0.83375	1	1	1	0.83979	-1.63276		128.46	
$\angle H C_1 H$	2.11106	2.11106	3.4232	-15.75493 C_1	7	H	H	0.83359	1	1	1	0.75	1.15796	0		108.44	107 (propane)
$\angle C_1 C_1 C_1$																112	
$\angle C_1 C_1 H$													69.51			110.49	113.8 (acetone)
$\angle C_1 C_1 H$													69.51			110.49	111.5 (acetone)
$\angle H C_1 H$	2.09711	2.09711	3.4232	-15.75493 C_1	7	H	H	0.83359	1	1	1	0.75	1.15796	0		108.50	108.5 (acetone)
$\angle C_1 C_1 C_1$																109.44	
$\angle C_1 C_1 H$													70.56			109.44	
$\angle C_1 C_1 C_1$	2.01547	2.01547	4.7958	-16.68412 C_1	25	-16.68412 C_2	25	0.81549	0.81549	1	1	1	0.81549	-1.83836		110.67	110.8 (acetone)
$\angle C_1 C_1 H$	2.01547	2.11323	4.1633	-15.55033 C_2	5	-14.82375 C_1	1	0.87495	0.91771	0.75	1	0.75	1.04887	0		110.76	
$\angle C_1 C_1 H$	2.01547	2.09711	4.1633	-15.55033 C_2	5	-14.82375 C_1	1	0.87495	0.91771	0.75	1	0.75	1.04887	0		111.27	111.4 (acetone)
$\angle C_1 C_1 C_1$	2.03327	2.03327	4.7938	-15.55033 C_1	5	-14.82375 C_2	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.83836		111.27	111.4 (acetone)
$\angle C_1 C_1 C_1$													72.59			107.50	

NITRILES ($C_nH_{2n-1}N$, $n = 2, 3, 4, 5 \dots \infty$)

The nitriles, $C_nH_{2n-1}N$, comprise a $C \equiv N$ functional group, and the single bond of carbon to the nitrile carbon atom, $C - CN$, is also a functional group. The alkyl portion of the nitrile may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C - C$ bonds can be identified. The n-alkane $C - C$ bond is the same as that of straight-chain alkanes. In addition, the $C - C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C - C$ bonds comprise functional groups. The branched-chain-alkane groups in nitriles are equivalent to those in branched-chain alkanes.

The nitrile $C \equiv N$ is solved equivalently to acetylene as given in the Acetylene Molecule section except that the energy for $\Delta E_{H_2MO}(AO/HO)$ is two times that given in Eq. (14.343), 16.20002 eV, in order to match the N AOs to that of the nitrile $C2sp^3$ HO having a bond order of three. $E_r(atom - atom, msp^3.AO)$ of the $C \equiv N$ functional group is -1.56513 eV (Eq. (14.342)) corresponding to the third-order bonded $C2sp^3$ HO.

The $C - CN$ functional group is equivalent to that of an alkyl $C - C$ group given in the Continuous-Chain Alkanes section except that $E_r(H, MO)$ and \bar{E}_{Kwb} are those corresponding to a nitrile. As given in the Continuous-Chain Alkanes section, $E_r(atom - atom, msp^3.AO)$ of the alkyl $C - C$ group is -1.85836 eV, where both energy contributions are given by Eq. (14.513). It is based on energy matching within the nitrile. It corresponds to the maximum-magnitude energy contributions of a single-bonded and a third-order bonded $C2sp^3$ HO.

The symbols of the functional groups of nitriles are given in Table 15.141. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of nitriles are given in Tables 15.142, 15.143, and 15.144, respectively. The total energy of each nitrile given in Table 15.139 was calculated as the sum over the integer multiple of each $E_D(group)$ of Table 15.144 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the

$E_D(\text{Group})$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of nitriles determined using Eqs. (15.79-15.108) are given in Table 15.146. The C of the $C \equiv N$ group can further bond with only one atom, and the bond is linear as a minimum of energy as in the case of acetylene and alkynes.

Table 15.141. The symbols of functional groups of nitriles.

Functional Group	Group Symbol
C-CN	C-C (i)
CN	C≡N
CH ₃ group	C-H (CH ₃)
CH ₂ group	C-H (CH ₂)
CH (alkyl) group	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (to iso-C)	C-C (e)
CC (to iso-C)	C-C (f)

Table 15.142. The geometrical bond parameters of nitriles and experimental values [1].

Parameter	C-C (i) Group	C≡N Group	C-H (CH ₃) Group	C-H (CH ₂) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
α (°)	1.91255	1.20590	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
ϵ' (°)	1.38295	1.09813	1.04856	1.05553	1.05661	1.45744	1.45744	1.42164	1.45744	1.45164	1.45164
Bond Length $2\epsilon'$ (Å)	1.46365	1.16221	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.468 (acetonitrile)	1.159 (acetonitrile)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
h, ϵ (°)	1.382110	0.49828	1.27293	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
α	0.72309	0.91064	0.63180	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15. (43). The MO to HO intercept geometrical bond parameters of nitriles. R, R', R'' are H or alkyl groups. E_T is $E_T(\text{atom-atom}, \text{exp}, \text{AO})$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy (Σ exp) (eV)	r_{bond} (a) (a)	E_{charge} (eV) Final	$E(\text{C2sp}^2)$ (eV) Final	θ (°)	θ_1 (°)	d_1 (a)	d_2 (a)
$RH_2C_2C_2 \equiv N$	N	-0.7837	0	0	0	-15.6032	0.8770	-15.6032	-15.6032	147.01	32.90	0.3669	0.7314
$RH_2C_2C_2 \equiv N$	C ₁	-0.7837	-0.92018	0	0	-15.32744	0.8272	-16.3750	-16.34664	146.42	34.58	0.42077	0.6796
$RH_2C_2C_2 \equiv N$	C ₂	-0.92018	-0.72437	0	0	-15.32744	0.8272	-16.3750	-16.34664	81.32	98.68	1.50718	0.12623
$RH_2C_2C_2 \equiv N$	C ₃	-0.92018	0	0	0	-15.34487	0.8039	-15.75493	-15.56407	83.50	94.50	1.45666	0.60771
$RH_2C_2C_2 \equiv N$	C ₄	-0.92018	-0.92018	0	0	-15.47406	0.81549	-16.6412	-16.9323	80.53	99.47	1.51718	0.13423
$R = \text{alkyl}$	C	-0.92018	0	0	0	-15.34487	0.8039	-15.75493	-15.56407	77.49	102.51	1.23564	0.18708
$C-H (CH_3)$	C	-0.92018	-0.92018	0	0	-15.47406	0.81549	-16.6412	-16.9323	68.47	111.53	1.35466	0.29933
$C-H (CH) (H)$	C	-0.92018	-0.92018	-0.92018	0	-15.40324	0.77247	-17.61330	-17.42244	61.10	118.90	1.42988	0.37226
$H_2C_2C_2H_2CH_3 -$ (C-C (a))	C ₁	-0.92018	0	0	0	-15.34487	0.8039	-15.75493	-15.56407	63.82	116.18	1.83879	0.38106
$H_2C_2C_2H_2CH_3 -$ (C-C (b))	C ₂	-0.92018	-0.92018	0	0	-15.47406	0.81549	-16.6412	-16.9323	56.41	123.59	1.90390	0.45117
$R-H_2C_2C_2(H_2C_2-R)HCH_3 -$ (C-C (a))	C ₁	-0.92018	-0.92018	-0.92018	0	-15.40324	0.77247	-17.61330	-17.42244	48.30	131.70	1.97162	0.51388
$R-H_2C_2C_2(R-H_2C_2)C_1(R'-H_2C_2)CH_3 -$ (C-C (b))	C ₂	-0.92018	-0.92018	-0.92018	-0.72437	-15.471860	0.75889	-17.92866	-17.73779	48.21	131.79	1.97344	0.50370
$H_2C_2C_2(H_2C_2-R)HCH_3 -$ (C-C (a))	C ₁	-0.92018	-0.92018	-0.92018	0	-15.40324	0.77247	-17.61330	-17.42244	48.30	131.70	1.97162	0.51388
$H_2C_2C_2(R-H_2C_2)C_1(R'-H_2C_2)CH_3 -$ (C-C (b))	C ₂	-0.92018	-0.92018	-0.92018	-0.72437	-15.451399	0.76763	-17.92866	-17.73779	50.04	129.96	1.94462	0.49298
$H_2C_2C_2(H_2C_2-R)HCH_3 -$ (C-C (a))	C ₁	-0.92018	-0.92018	-0.92018	0	-15.40324	0.77247	-17.61330	-17.42244	48.30	131.70	1.97162	0.51388
$H_2C_2C_2(R-H_2C_2)C_1(R'-H_2C_2)CH_3 -$ (C-C (b))	C ₂	-0.92018	-0.92018	-0.92018	-0.72437	-15.451399	0.76763	-17.92866	-17.73779	50.04	129.96	1.94462	0.49298
$H_2C_2C_2(R-H_2C_2)C_1(R'-H_2C_2)CH_3 -$ (C-C (b))	C ₁	-0.92018	-0.92018	-0.92018	-0.72437	-15.451399	0.76763	-17.92866	-17.73779	50.04	129.96	1.94462	0.49298

Table 15.144. The energy parameters (eV) of functional groups of nitriles.

Parameters	C-C (f) Group	C=N Group	C ₂ H ₅ Group	CH ₃ Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
R_1	1	3	2	1	1	1	1	1	1	1	1
R_2	0	0	2	1	0	0	0	0	0	0	0
R_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1
C_3	1	1	1	1	1	1	1	1	1	1	1
C_4	0.91771	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
C_5	2	6	1	1	1	2	2	2	2	2	2
C_6	0	0	3	2	1	0	0	0	0	0	0
C_7	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_8	1	1	1	1	1	1	1	1	1	1	1
P_1 (eV)	-33.01231	-207.49229	-107.32728	-70.41425	-33.12015	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214
V_1 (eV)	9.83824	37.16984	38.92728	25.78002	12.87680	9.33552	9.33552	9.33552	9.33552	9.33552	9.33552
T (eV)	8.63043	86.03250	32.53914	21.06675	10.48582	6.77464	6.77464	6.77464	6.77464	6.77464	6.77464
V_2 (eV)	-4.31522	-43.01625	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732
$E_{1,2,3,4,5,6,7,8}$ (eV)	-14.63489	32.40004	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{1,2,3,4,5,6,7,8}$ (eV)	-1.85837	0	0	0	0	0	0	0	0	0	0
E_1 (eV)	-12.77652	32.40004	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
E_2 (eV)	-31.03537	-94.90616	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537
E_3 (eV)	-1.85836	-1.56513	0	0	0	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836
E_4 (eV)	-33.49374	-96.47124	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373
ω (10 ⁶ rad/s)	19.2516	22.0753	24.9286	24.2751	24.1759	9.43699	9.43699	9.43699	9.43699	9.43699	9.43699
E_5 (eV)	12.67172	14.53031	16.40846	15.97831	15.91299	6.21159	6.21159	6.21159	6.21159	6.21159	6.21159
E_6 (eV)	-0.23588	-0.24250	-0.23532	-0.23017	-0.24966	-0.16515	-0.16515	-0.16515	-0.16515	-0.16515	-0.16515
$E_{1,2,3,4,5,6,7,8}$ (eV)	0.11407	0.28107	0.35532	0.35532	0.35532	0.12312	0.12312	0.12312	0.12312	0.12312	0.12312
E_7 (eV)	-0.17884	-0.10197	-0.22757	-0.14502	-0.07200	-0.10359	-0.10359	-0.10359	-0.10359	-0.10359	-0.10359
E_8 (eV)	0.14803	0.14185	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E_9 (eV)	-33.67258	-96.77713	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732
$E_{1,2,3,4,5,6,7,8}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{1,2,3,4,5,6,7,8}$ (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{1,2,3,4,5,6,7,8}$ (eV)	4.40280	8.87594	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

THIOLS ($C_nH_{2n+2}S_m$, $n=1,2,3,4,5\ldots\infty$)

The alkyl thiols, $C_nH_{2n+2}S_m$, comprise a SH functional group and a $C-S$ functional group. The alkyl portion of the alkyl thiol may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n -alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t -butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t -butyl, and t -butyl to t -butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in thiols are equivalent to those in branched-chain alkanes.

The parameters of the SH functional group is solved using Eq. (15.41). As in the case of the $C-H$ bonds of CH_n , $n=1,2,3$, the $S-H$ -bond MO is a partial prolate spheroid in between the sulfur and hydrogen nuclei and is continuous with the $S3p$ shell. The energy of the H_2 -type ellipsoidal MO is matched to that of the $S3p$ shell and comprises 75% of a H_2 -type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Since the energy of S , $E(S) = -10.36001 \text{ eV}$, is less than that of H , the linear combination of the H_2 -type ellipsoidal MO with the $S3p$ shell further comprises an excess 50% charge-density donation from H to the $S3p$ shell of the $S-H$ -bond MO to achieve an energy minimum. The initial total energy of the shell is given by the sum over the four $3p$ electrons. From Eq. (15.12), the sum $E_T(S, 3p)$ of the energies of S , S^+ , S^{2+} , and S^{3+} [38] is

$$\begin{aligned} E_T(S, 3p) &= 10.36001 \text{ eV} + 23.33788 \text{ eV} + 34.79 \text{ eV} + 47.222 \text{ eV} \\ &= 115.70989 \text{ eV} \end{aligned} \quad (15.118)$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius r_{3p} of the $S3p$ shell may be calculated from the Coulombic energy using Eqs. (15.13) and (15.118):

$$r_{3p} = \sum_{q=12}^{15} \frac{(Z-q)e^2}{8\pi\epsilon_0(e115.70989 \text{ eV})} = \frac{10e^2}{8\pi\epsilon_0(e115.70989 \text{ eV})} = 1.17585a_0 \quad (15.119)$$

where $Z=16$ for sulfur. Using Eqs. (15.14) and (15.119), the Coulombic energy $E_{Coulomb}(S, 3p)$ of the outer electron of the $S3p$ shell is

$$E_{Coulomb}(S, 3p) = \frac{-e^2}{8\pi\epsilon_0 r_{3p}} = \frac{-e^2}{8\pi\epsilon_0 1.17585a_0} = -11.57099 \text{ eV} \quad (15.120)$$

The sharing of the electrons between the S and H atoms permits the formation an $S-H$ bond MO that is lowered more in energy than the participating $S3p$ orbital which consequently increases in energy. By considering the 50% electron redistribution in the $S-H$ group as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius r_{S-H3p} of the $S3p$ shell may be calculated from the Coulombic energy using Eq. (15.18)

$$\begin{aligned} r_{S-H3p} &= \left(\sum_{n=12}^{15} (Z-n) + 0.25 \right) \frac{e^2}{8\pi\epsilon_0 (e115.70989 \text{ eV})} \\ &= \frac{10.5e^2}{8\pi\epsilon_0 (e115.70989 \text{ eV})} \\ &= 1.23465a_0 \end{aligned} \quad (15.121)$$

where the $s=-1$ in Eq. (15.18) due to the charge donation from H to S . Using Eqs. (15.19) and (15.121), the Coulombic energy $E_{Coulomb}(S_{S-H}, 3p)$ of the outer electron of the $S3p$ shell is

$$\begin{aligned} E_{Coulomb}(S_{S-H}, 3p) &= \frac{-e^2}{8\pi\epsilon_0 r_{S-H3p}} \\ &= \frac{-e^2}{8\pi\epsilon_0 1.23465a_0} \\ &= -11.01999 \text{ eV} \end{aligned} \quad (15.122)$$

Thus, $E_T(S-H, 3p)$, the energy change of each $S3p$ shell with the formation of the $S-H$ bond MO is given by the difference between Eq. (15.120) and Eq. (15.122):

$$\begin{aligned} E_T(S-H, 3p) &= E(S_{S-H}, 3p) - E(S, 3p) \\ &= -11.01999 \text{ eV} - (-11.57099 \text{ eV}) \\ &= 0.55100 \text{ eV} \end{aligned} \quad (15.123)$$

15 Then, in Eq. (15.42):

$$\begin{aligned} E_T(AO/HO) &= E(S) - E_T(S-H, 3p) \\ &= -10.36001 \text{ eV} - 0.55100 \text{ eV} \\ &= -10.91101 \text{ eV} \end{aligned} \quad (15.124)$$

And, in Eq. (15.56),

$$E_T(\text{atom} - \text{atom}, msp^3, AO) = 0.55100 \text{ eV} \quad (15.125)$$

Due to the charge donation from H to S , $c_1 = 1$ in both Eqs. (15.42) and (15.56). As in the case of the $C-H$ -bond MO, $C_1 = 0.75$ based on the orbital composition. In alkyl thiols, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is also one, and the energy matching condition is determined by the C_2 parameter. Using the energy of S , $E(S) = -10.36001 \text{ eV}$ in Eq. (15.65), the hybridization factor C_2 of Eq. (15.52) for the $S-H$ -bond MO is

$$C_2(S3p \text{ to } H) = \frac{E(S, 3p)}{E(H)} = \frac{-10.36001 \text{ eV}}{-13.60580 \text{ eV}} = 0.76144 \quad (15.126)$$

Since the energy of S is matched to the Coulombic energy between the electron and proton of

$$H, \quad E(H(a_0)), \quad E_{\text{initial}}(c_1 \text{ AO/HO}) = E(H(a_0)) = -13.60580 \text{ eV},$$

10 $E_{\text{initial}}(c_1 \text{ AO/HO}) = E(H) = -13.59844 \text{ eV}$, and E_{mag} is that corresponding to $E(H(a_0))$ given by Eq. (15.58). $E_D(\text{Group})$ for hydrogen sulfide is equivalent to that of the SH functional group, and the $E_D(\text{Group})$ (eV) for dihydrogen sulfide follows the same derivation as that for the SH functional group except that the parameters correspond to $n_1 = 2$ rather than $n_1 = 1$ in Eqs. (15.42) and (15.56).

15 Furthermore, with the energy of S matched to the Coulombic energy between the electron and proton of H , the energy of the $C-S$ -bond MO is the sum of the component energies of the H_2 -type ellipsoidal MO given in Eq. (15.42) with $E(\text{AO/HO}) = 0$ and $E_T(\text{AO/HO}) = \Delta E_{H_2 \text{ MO}}(\text{AO/HO})$. Then, the solution of the $C-S$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of C to form a single $2sp^3$ shell as an

20 energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the S AO to form a MO permits each participating orbital to decrease in radius and energy. Since the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243), c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. Then, $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a

25 corresponding energy of $E(C, 2sp^3) = -14.63489 \text{ eV}$ (Eq. (15.25)), and the S AO has an energy of $E(S) = -10.36001 \text{ eV}$. To meet the equipotential condition of the union of the

$C-S$ H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.51) for the $C-S$ -bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3HO \text{ to } S) = \frac{E(S)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-10.36001 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.64965 \quad (15.127)$$

Since the sulfur is energy matched to $E(H(a_0))$ in the $S-H$ -bond MO,

- 5 $E_r(atom - atom, msp^3 AO)$ of the $C-S$ -bond MO in Eq. (15.52) due to the charge donation from the C and S atoms to the MO is -0.72457 eV corresponding to the energy contribution equivalent to that of a methyl group (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl thiols are given in Table 15.147. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and
10 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl thiols are given in Tables 15.148, 15.149, and 15.150, respectively. The total energy of each alkyl thiol given in Table 15.151 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.150 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted
15 from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The $C-C$ bonds to the $HCSH$ group (one H bond to C) were each treated as an iso $C-C$ bond. The $C-C$ bonds to the CSH group (no H bonds to C) were each treated as a tert-butyl $C-C$. E_{mag} was subtracted for each t-butyl group. The bond angle parameters of alkyl thiols determined using Eqs. (15.79-15.108) are given in Table 15.152.

Table 13.147. The symbols of functional groups of alkyl thiols.

Functional Group	SH Group Symbol
SH group	H_2S
C-S	$C-S$
CH ₃ group	$C-H (CH_3)$
CH ₂ group	$C-H (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C (a)$
CC bond (iso-C)	$C-C (b)$
CC bond (tert-C)	$C-C (c)$
CC (iso to iso-C)	$C-C (d)$
CC (t to i-C)	$C-C (e)$
CC (t to iso-C)	$C-C (f)$

Table 13.148. The geometrical bond parameters of alkyl thiols and experimental values [1].

Parameter	$S-H (H_2S)$	SH Group	$C-S$ Group	$C-H (CH_3)$ Group	$C-H (CH_2)$ Group	$C-H$ Group	$C-C (a)$ Group	$C-C (b)$ Group	$C-C (c)$ Group	$C-C (d)$ Group	$C-C (e)$ Group	$C-C (f)$ Group
$a (a_0)$	1.83762	1.83762	1.90975	1.64920	1.67122	1.67463	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c' (a_0)$	1.26942	1.26842	1.71455	1.04856	1.05353	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length	1.34244	1.34244	1.81460	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
$2c' (A)$	1.34066	1.34066	1.819	1.107	1.107	1.122	1.532	1.532	1.532	1.532	1.532	1.532
Exp. Bond Length	1.3356	(hydrogen sulfide)	(methanethiol)	(C-H propane)	(C-H propane)	(isobutane)	(propane)	(propane)	(propane)	(propane)	(propane)	(propane)
A	1.34	1.34	1.829	1.117	1.117	1.122	1.531	1.531	1.531	1.531	1.531	1.531
$b, c (a_0)$	1.32964	1.32964	0.84112	1.27295	1.25569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
a	0.69025	0.69025	0.89778	0.63380	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.149. The MO to HO intercept geometrical bond parameters of alkyl thiols. E_i is $E_i(\text{atom} - \text{atom}_i, \text{mol}^2, \text{AC})$.

Bond	Atom	E_i (eV) Bond 1	E_i (eV) Bond 2	E_i (eV) Bond 3	E_i (eV) Bond 4	Final Total Energy (eV)	r_{atom} (a.u.)	r_{mol} (a.u.)	E_{atom} Final	E_{mol} Final	θ_i (°)	θ_j (°)	d_i (a.u.)	d_j (a.u.)
N-H (hydrogen sulfide)	N	0.55100	0	0	0		1.32010	1.33463	-11.01099		71.33	61.62	0.87355	0.39487
NS-H	N	-0.36229	0.55100	0	0		1.32010	0.92553	-14.63704		92.91	44.38	1.11557	0.84714
C-H ₁ -SH	N	-0.36229	0.55100	0	0		1.32010	0.92553	-14.63704		47.94	53.13	1.09181	0.82294
C-H ₂ -SH	C	-0.36229	0	0	0	-151.97798	0.91771	0.85582	-15.18004	-14.99117	110.16	98.87	0.93762	1.67692
RR'-H ₁ C ₁ H ₂ -C ₁ H ₁ SH	C	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.93656	51.31	51.57	1.18689	0.52765
C-H (CH ₃)	C	-0.92918	0	0	0	-153.44487	0.91771	0.86359	-15.74493	-15.56407	102.51	41.48	1.23564	0.18708
C-H (CH ₂)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	111.53	33.84	1.34486	0.30933
C-H (CH)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	118.90	31.37	1.42988	0.37526
H ₁ C ₁ C ₂ H ₂ CH ₃ - (C-C (b))	C	-0.92918	0	0	0	-153.54487	0.91771	0.86359	-15.74493	-15.56407	116.18	30.08	1.33879	0.38106
H ₁ C ₁ C ₂ H ₂ CH ₃ - (C-C (b))	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	123.59	26.06	1.90050	0.45117
R-H ₁ C ₁ C ₂ (H ₁ C ₁ -R')HCH ₃ - (C-C (b))	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	131.70	21.90	1.97102	0.51388
R-H ₁ C ₁ C ₂ (R'-H ₁ C ₁)(C ₁ (R'-H ₁ C ₁))CH ₃ - (C-C (b))	C	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.73589	-17.92866	-17.73779	131.79	21.74	1.95754	0.50570
RR'-H ₁ C ₁ C ₂ (H ₁ C ₁ -R')HCH ₃ - (C-C (b))	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	131.70	21.90	1.97102	0.51388
RR'-H ₁ C ₁ C ₂ (R'-H ₁ C ₁)(C ₁ (R'-H ₁ C ₁))CH ₃ - (C-C (b))	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76763	-17.93866	-17.73779	129.96	22.66	1.84462	0.48298
RR'-H ₁ C ₁ C ₂ (H ₁ C ₁ -R')HCH ₃ - (C-C (b))	C	-0.72457	-0.92918	-0.92918	0	-154.10463	0.91771	0.78155	-17.42869	-17.21783	127.22	24.04	1.93443	0.47279
RR'-H ₁ C ₁ C ₂ (R'-H ₁ C ₁)(C ₁ (R'-H ₁ C ₁))CH ₃ - (C-C (b))	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76763	-17.92866	-17.73779	129.96	22.66	1.84462	0.48298

Table 15.150. The energy parameters (eV) of functional groups of alkyl (thio).

Parameters	H_{2s}^*	σH	$C-H$	$C-H_2$	$C-H_3$	$C-H$	$C-C$	$C-C$	$C-C$	$C-C$	$C-C$	$C-C$
Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
H_1	2	1	1	3	2	1	1	1	1	1	1	1
H_2	0	0	0	2	1	0	0	0	0	0	0	0
H_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5
C_2	0.76144	0.76144	0.64965	1	1	1	1	1	1	1	1	1
C_3	1	1	1	1	1	1	1	1	1	1	1	1
C_4	1	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
C_5	2	1	0	0	1	1	2	2	2	2	2	2
C_6	1	1	0	3	2	1	0	0	0	0	0	0
C_7	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5
C_8	0.76144	0.76144	0.64965	1	1	1	1	1	1	1	1	1
C_9	-72.80662	-36.40331	-46.36405	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214
C_{10}	21.43310	10.72655	7.93551	38.92728	25.78002	12.87680	9.33352	9.33352	9.33352	9.33352	9.33352	9.33352
C_{11}	19.81003	9.90502	12.13899	32.53914	21.06675	10.48352	6.77464	6.77464	6.77464	6.77464	6.77464	6.77464
C_{12}	-9.90502	-4.95251	-6.05949	-16.26557	-10.53337	-5.24291	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732
C_{13}	-20.72002	-10.36001	0	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
C_{14}	1.10200	0.55100	-0.72457	0	0	0	0	0	0	0	0	0
C_{15}	-19.61802	-10.91101	0.72457	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
C_{16}	-63.27032	-31.63526	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537
C_{17}	1.10200	0.55100	-0.72457	0	0	0	0	0	0	0	0	0
C_{18}	-62.16874	-31.08437	-32.35994	-67.69450	-49.66493	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537
C_{19}	12.4415	12.5415	30.5436	24.9786	24.2751	24.1759	9.43699	9.43699	9.43699	9.43699	9.43699	9.43699
C_{20}	8.25504	8.25504	20.10634	16.40846	15.97831	15.91259	6.21159	6.21159	6.21159	6.21159	6.21159	6.21159
C_{21}	-0.17669	-0.17669	-0.28705	-0.25532	-0.24017	-0.24066	-0.16515	-0.16515	-0.16515	-0.16515	-0.16515	-0.16515
C_{22}	0.32472	0.32472	0.08146	0.35532	0.35532	0.35532	0.12312	0.12312	0.12312	0.12312	0.12312	0.12312
C_{23}	-0.01458	-0.01458	-0.24652	-0.22757	-0.14502	-0.07200	-0.10359	-0.10359	-0.10359	-0.10359	-0.10359	-0.10359
C_{24}	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
C_{25}	-31.10493	-31.09296	-32.60616	-67.97207	-49.60996	-31.70737	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732
C_{26}	-13.60580	-13.60580	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
C_{27}	-13.59844	-13.59844	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
C_{28}	3.78628	3.77430	3.33448	12.49186	7.83016	3.32601	4.32754	4.29921	4.29921	4.29921	4.29921	4.29921
C_{29}	63.19789	63.19789	63.19789	63.19789	63.19789	63.19789	63.19789	63.19789	63.19789	63.19789	63.19789	63.19789

 $\Delta E_{1/2} = E_{1/2}(H_2) - E_{1/2}(H_1) = 63.19789 \text{ eV} - (-31.09296 \text{ eV})$

Table 15.151. The total bond energies of alkyl thiols calculated using the functional group composition and the energies of Table 15.150 compared to the experimental values E_{exp} that is subtracted from the weighted sum of the E_{g} (kJ mol^{-1}) values base composition is given by (15.58).

Name	H_2S Group	SH Group	$C-S$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{exp}	Calculated Total Bond Energy (kJ)	Experimental Total Bond Energy (kJ)	Relative Error
H_2S	1													2.63	2.63	-0.0370
CH_3S	1	1												19.67	19.67	-0.0000
CH_3SH	1	1	1											19.67	19.67	-0.0000
CH_3S	1	1	1	1										31.76	31.76	-0.0000
CH_3SH	1	1	1	1	1									43.93	43.93	-0.0000
CH_3S	1	1	1	1	1	1								44.03	44.03	-0.0000
CH_3SH	1	1	1	1	1	1	1							56.07	56.07	-0.0000
CH_3S	1	1	1	1	1	1	1	1						56.18	56.18	-0.0000
CH_3SH	1	1	1	1	1	1	1	1	1					68.26	68.26	-0.0000
CH_3S	1	1	1	1	1	1	1	1	1	1				68.31	68.31	-0.0000
CH_3SH	1	1	1	1	1	1	1	1	1	1	1			80.41	80.41	-0.0000
CH_3S	1	1	1	1	1	1	1	1	1	1	1	1		80.46	80.46	-0.0000
CH_3SH	1	1	1	1	1	1	1	1	1	1	1	1		92.56	92.56	-0.0000
CH_3S	1	1	1	1	1	1	1	1	1	1	1	1		92.61	92.61	-0.0000
CH_3SH	1	1	1	1	1	1	1	1	1	1	1	1		104.71	104.71	-0.0000
CH_3S	1	1	1	1	1	1	1	1	1	1	1	1		104.76	104.76	-0.0000
CH_3SH	1	1	1	1	1	1	1	1	1	1	1	1		116.86	116.86	-0.0000
CH_3S	1	1	1	1	1	1	1	1	1	1	1	1		116.91	116.91	-0.0000
CH_3SH	1	1	1	1	1	1	1	1	1	1	1	1		128.96	128.96	-0.0000
CH_3S	1	1	1	1	1	1	1	1	1	1	1	1		129.01	129.01	-0.0000

Table 15.152. The bond angle parameters of alkyl thiols and experimental values [1]. In the calculation of θ_i , the parameters from the preceding angle were used. E_i is $E_i(\text{atom} - \text{atom} - \text{exp} - \text{AO})$.

Name of Angle	$2C_1$ Bond 1 (θ_1)	$2C_2$ Bond 2 (θ_2)	$2C_3$ Bond 3 (θ_3)	$2C_4$ Bond 4 (θ_4)	$2C_5$ Bond 5 (θ_5)	$2C_6$ Bond 6 (θ_6)	$2C_7$ Bond 7 (θ_7)	$2C_8$ Bond 8 (θ_8)	$2C_9$ Bond 9 (θ_9)	$2C_{10}$ Bond 10 (θ_{10})	$2C_{11}$ Bond 11 (θ_{11})	$2C_{12}$ Bond 12 (θ_{12})	$2C_{13}$ Bond 13 (θ_{13})	$2C_{14}$ Bond 14 (θ_{14})	$2C_{15}$ Bond 15 (θ_{15})	$2C_{16}$ Bond 16 (θ_{16})	$2C_{17}$ Bond 17 (θ_{17})	$2C_{18}$ Bond 18 (θ_{18})	$2C_{19}$ Bond 19 (θ_{19})	$2C_{20}$ Bond 20 (θ_{20})	$2C_{21}$ Bond 21 (θ_{21})	$2C_{22}$ Bond 22 (θ_{22})	$2C_{23}$ Bond 23 (θ_{23})	$2C_{24}$ Bond 24 (θ_{24})	$2C_{25}$ Bond 25 (θ_{25})	$2C_{26}$ Bond 26 (θ_{26})	$2C_{27}$ Bond 27 (θ_{27})	$2C_{28}$ Bond 28 (θ_{28})	$2C_{29}$ Bond 29 (θ_{29})	$2C_{30}$ Bond 30 (θ_{30})	$2C_{31}$ Bond 31 (θ_{31})	$2C_{32}$ Bond 32 (θ_{32})	$2C_{33}$ Bond 33 (θ_{33})	$2C_{34}$ Bond 34 (θ_{34})	$2C_{35}$ Bond 35 (θ_{35})	$2C_{36}$ Bond 36 (θ_{36})	$2C_{37}$ Bond 37 (θ_{37})	$2C_{38}$ Bond 38 (θ_{38})	$2C_{39}$ Bond 39 (θ_{39})	$2C_{40}$ Bond 40 (θ_{40})	$2C_{41}$ Bond 41 (θ_{41})	$2C_{42}$ Bond 42 (θ_{42})	$2C_{43}$ Bond 43 (θ_{43})	$2C_{44}$ Bond 44 (θ_{44})	$2C_{45}$ Bond 45 (θ_{45})	$2C_{46}$ Bond 46 (θ_{46})	$2C_{47}$ Bond 47 (θ_{47})	$2C_{48}$ Bond 48 (θ_{48})	$2C_{49}$ Bond 49 (θ_{49})	$2C_{50}$ Bond 50 (θ_{50})	$2C_{51}$ Bond 51 (θ_{51})	$2C_{52}$ Bond 52 (θ_{52})	$2C_{53}$ Bond 53 (θ_{53})	$2C_{54}$ Bond 54 (θ_{54})	$2C_{55}$ Bond 55 (θ_{55})	$2C_{56}$ Bond 56 (θ_{56})	$2C_{57}$ Bond 57 (θ_{57})	$2C_{58}$ Bond 58 (θ_{58})	$2C_{59}$ Bond 59 (θ_{59})	$2C_{60}$ Bond 60 (θ_{60})	$2C_{61}$ Bond 61 (θ_{61})	$2C_{62}$ Bond 62 (θ_{62})	$2C_{63}$ Bond 63 (θ_{63})	$2C_{64}$ Bond 64 (θ_{64})	$2C_{65}$ Bond 65 (θ_{65})	$2C_{66}$ Bond 66 (θ_{66})	$2C_{67}$ Bond 67 (θ_{67})	$2C_{68}$ Bond 68 (θ_{68})	$2C_{69}$ Bond 69 (θ_{69})	$2C_{70}$ Bond 70 (θ_{70})	$2C_{71}$ Bond 71 (θ_{71})	$2C_{72}$ Bond 72 (θ_{72})	$2C_{73}$ Bond 73 (θ_{73})	$2C_{74}$ Bond 74 (θ_{74})	$2C_{75}$ Bond 75 (θ_{75})	$2C_{76}$ Bond 76 (θ_{76})	$2C_{77}$ Bond 77 (θ_{77})	$2C_{78}$ Bond 78 (θ_{78})	$2C_{79}$ Bond 79 (θ_{79})	$2C_{80}$ Bond 80 (θ_{80})	$2C_{81}$ Bond 81 (θ_{81})	$2C_{82}$ Bond 82 (θ_{82})	$2C_{83}$ Bond 83 (θ_{83})	$2C_{84}$ Bond 84 (θ_{84})	$2C_{85}$ Bond 85 (θ_{85})	$2C_{86}$ Bond 86 (θ_{86})	$2C_{87}$ Bond 87 (θ_{87})	$2C_{88}$ Bond 88 (θ_{88})	$2C_{89}$ Bond 89 (θ_{89})	$2C_{90}$ Bond 90 (θ_{90})	$2C_{91}$ Bond 91 (θ_{91})	$2C_{92}$ Bond 92 (θ_{92})	$2C_{93}$ Bond 93 (θ_{93})	$2C_{94}$ Bond 94 (θ_{94})	$2C_{95}$ Bond 95 (θ_{95})	$2C_{96}$ Bond 96 (θ_{96})	$2C_{97}$ Bond 97 (θ_{97})	$2C_{98}$ Bond 98 (θ_{98})	$2C_{99}$ Bond 99 (θ_{99})	$2C_{100}$ Bond 100 (θ_{100})	$2C_{101}$ Bond 101 (θ_{101})	$2C_{102}$ Bond 102 (θ_{102})	$2C_{103}$ Bond 103 (θ_{103})	$2C_{104}$ Bond 104 (θ_{104})	$2C_{105}$ Bond 105 (θ_{105})	$2C_{106}$ Bond 106 (θ_{106})	$2C_{107}$ Bond 107 (θ_{107})	$2C_{108}$ Bond 108 (θ_{108})	$2C_{109}$ Bond 109 (θ_{109})	$2C_{110}$ Bond 110 (θ_{110})	$2C_{111}$ Bond 111 (θ_{111})	$2C_{112}$ Bond 112 (θ_{112})	$2C_{113}$ Bond 113 (θ_{113})	$2C_{114}$ Bond 114 (θ_{114})	$2C_{115}$ Bond 115 (θ_{115})	$2C_{116}$ Bond 116 (θ_{116})	$2C_{117}$ Bond 117 (θ_{117})	$2C_{118}$ Bond 118 (θ_{118})	$2C_{119}$ Bond 119 (θ_{119})	$2C_{120}$ Bond 120 (θ_{120})	$2C_{121}$ Bond 121 (θ_{121})	$2C_{122}$ Bond 122 (θ_{122})	$2C_{123}$ Bond 123 (θ_{123})	$2C_{124}$ Bond 124 (θ_{124})	$2C_{125}$ Bond 125 (θ_{125})	$2C_{126}$ Bond 126 (θ_{126})	$2C_{127}$ Bond 127 (θ_{127})	$2C_{128}$ Bond 128 (θ_{128})	$2C_{129}$ Bond 129 (θ_{129})	$2C_{130}$ Bond 130 (θ_{130})	$2C_{131}$ Bond 131 (θ_{131})	$2C_{132}$ Bond 132 (θ_{132})	$2C_{133}$ Bond 133 (θ_{133})	$2C_{134}$ Bond 134 (θ_{134})	$2C_{135}$ Bond 135 (θ_{135})	$2C_{136}$ Bond 136 (θ_{136})	$2C_{137}$ Bond 137 (θ_{137})	$2C_{138}$ Bond 138 (θ_{138})	$2C_{139}$ Bond 139 (θ_{139})	$2C_{140}$ Bond 140 (θ_{140})	$2C_{141}$ Bond 141 (θ_{141})	$2C_{142}$ Bond 142 (θ_{142})	$2C_{143}$ Bond 143 (θ_{143})	$2C_{144}$ Bond 144 (θ_{144})	$2C_{145}$ Bond 145 (θ_{145})	$2C_{146}$ Bond 146 (θ_{146})	$2C_{147}$ Bond 147 (θ_{147})	$2C_{148}$ Bond 148 (θ_{148})	$2C_{149}$ Bond 149 (θ_{149})	$2C_{150}$ Bond 150 (θ_{150})	$2C_{151}$ Bond 151 (θ_{151})	$2C_{152}$ Bond 152 (θ_{152})	$2C_{153}$ Bond 153 (θ_{153})	$2C_{154}$ Bond 154 (θ_{154})	$2C_{155}$ Bond 155 (θ_{155})	$2C_{156}$ Bond 156 (θ_{156})	$2C_{157}$ Bond 157 (θ_{157})	$2C_{158}$ Bond 158 (θ_{158})	$2C_{159}$ Bond 159 (θ_{159})	$2C_{160}$ Bond 160 (θ_{160})	$2C_{161}$ Bond 161 (θ_{161})	$2C_{162}$ Bond 162 (θ_{162})	$2C_{163}$ Bond 163 (θ_{163})	$2C_{164}$ Bond 164 (θ_{164})	$2C_{165}$ Bond 165 (θ_{165})	$2C_{166}$ Bond 166 (θ_{166})	$2C_{167}$ Bond 167 (θ_{167})	$2C_{168}$ Bond 168 (θ_{168})	$2C_{169}$ Bond 169 (θ_{169})	$2C_{170}$ Bond 170 (θ_{170})	$2C_{171}$ Bond 171 (θ_{171})	$2C_{172}$ Bond 172 (θ_{172})	$2C_{173}$ Bond 173 (θ_{173})	$2C_{174}$ Bond 174 (θ_{174})	$2C_{175}$ Bond 175 (θ_{175})	$2C_{176}$ Bond 176 (θ_{176})	$2C_{177}$ Bond 177 (θ_{177})	$2C_{178}$ Bond 178 (θ_{178})	$2C_{179}$ Bond 179 (θ_{179})	$2C_{180}$ Bond 180 (θ_{180})	$2C_{181}$ Bond 181 (θ_{181})	$2C_{182}$ Bond 182 (θ_{182})	$2C_{183}$ Bond 183 (θ_{183})	$2C_{184}$ Bond 184 (θ_{184})	$2C_{185}$ Bond 185 (θ_{185})	$2C_{186}$ Bond 186 (θ_{186})	$2C_{187}$ Bond 187 (θ_{187})	$2C_{188}$ Bond 188 (θ_{188})	$2C_{189}$ Bond 189 (θ_{189})	$2C_{190}$ Bond 190 (θ_{190})	$2C_{191}$ Bond 191 (θ_{191})	$2C_{192}$ Bond 192 (θ_{192})	$2C_{193}$ Bond 193 (θ_{193})	$2C_{194}$ Bond 194 (θ_{194})	$2C_{195}$ Bond 195 (θ_{195})	$2C_{196}$ Bond 196 (θ_{196})	$2C_{197}$ Bond 197 (θ_{197})	$2C_{198}$ Bond 198 (θ_{198})	$2C_{199}$ Bond 199 (θ_{199})	$2C_{200}$ Bond 200 (θ_{200})	$2C_{201}$ Bond 201 (θ_{201})	$2C_{202}$ Bond 202 (θ_{202})	$2C_{203}$ Bond 203 (θ_{203})	$2C_{204}$ Bond 204 (θ_{204})	$2C_{205}$ Bond 205 (θ_{205})	$2C_{206}$ Bond 206 (θ_{206})	$2C_{207}$ Bond 207 (θ_{207})	$2C_{208}$ Bond 208 (θ_{208})	$2C_{209}$ Bond 209 (θ_{209})	$2C_{210}$ Bond 210 (θ_{210})	$2C_{211}$ Bond 211 (θ_{211})	$2C_{212}$ Bond 212 (θ_{212})	$2C_{213}$ Bond 213 (θ_{213})	$2C_{214}$ Bond 214 (θ_{214})	$2C_{215}$ Bond 215 (θ_{215})	$2C_{216}$ Bond 216 (θ_{216})	$2C_{217}$ Bond 217 (θ_{217})	$2C_{218}$ Bond 218 (θ_{218})	$2C_{219}$ Bond 219 (θ_{219})	$2C_{220}$ Bond 220 (θ_{220})	$2C_{221}$ Bond 221 (θ_{221})	$2C_{222}$ Bond 222 (θ_{222})	$2C_{223}$ Bond 223 (θ_{223})	$2C_{224}$ Bond 224 (θ_{224})	$2C_{225}$ Bond 225 (θ_{225})	$2C_{226}$ Bond 226 (θ_{226})	$2C_{227}$ Bond 227 (θ_{227})	$2C_{228}$ Bond 228 (θ_{228})	$2C_{229}$ Bond 229 (θ_{229})	$2C_{230}$ Bond 230 (θ_{230})	$2C_{231}$ Bond 231 (θ_{231})	$2C_{232}$ Bond 232 (θ_{232})	$2C_{233}$ Bond 233 (θ_{233})	$2C_{234}$ Bond 234 (θ_{234})	$2C_{235}$ Bond 235 (θ_{235})	$2C_{236}$ Bond 236 (θ_{236})	$2C_{237}$ Bond 237 (θ_{237})	$2C_{238}$ Bond 238 (θ_{238})	$2C_{239}$ Bond 239 (θ_{239})	$2C_{240}$ Bond 240 (θ_{240})	$2C_{241}$ Bond 241 (θ_{241})	$2C_{242}$ Bond 242 (θ_{242})	$2C_{243}$ Bond 243 (θ_{243})	$2C_{244}$ Bond 244 (θ_{244})	$2C_{245}$ Bond 245 (θ_{245})	$2C_{246}$ Bond 246 (θ_{246})	$2C_{247}$ Bond 247 (θ_{247})	$2C_{248}$ Bond 248 (θ_{248})	$2C_{249}$ Bond 249 (θ_{249})	$2C_{250}$ Bond 250 (θ_{250})	$2C_{251}$ Bond 251 (θ_{251})	$2C_{252}$ Bond 252 (θ_{252})	$2C_{253}$ Bond 253 (θ_{253})	$2C_{254}$ Bond 254 (θ_{254})	$2C_{255}$ Bond 255 (θ_{255})	$2C_{256}$ Bond 256 (θ_{256})	$2C_{257}$ Bond 257 (θ_{257})	$2C_{258}$ Bond 258 (θ_{258})	$2C_{259}$ Bond 259 (θ_{259})	$2C_{260}$ Bond 260 (θ_{260})	$2C_{261}$ Bond 261 (θ_{261})	$2C_{262}$ Bond 262 (θ_{262})	$2C_{263}$ Bond 263 (θ_{263})	$2C_{264}$ Bond 264 (θ_{264})	$2C_{265}$ Bond 265 (θ_{265})	$2C_{266}$ Bond 266 (θ_{266})	$2C_{267}$ Bond 267 (θ_{267})	$2C_{268}$ Bond 268 (θ_{268})	$2C_{269}$ Bond 269 (θ_{269})	$2C_{270}$ Bond 270 (θ_{270})	$2C_{271}$ Bond 271 (θ_{271})	$2C_{272}$ Bond 272 (θ_{272})	$2C_{273}$ Bond 273 (θ_{273})	$2C_{274}$ Bond 274 (θ_{274})	$2C_{275}$ Bond 275 (θ_{275})	$2C_{276}$ Bond 276 (θ_{276})	$2C_{277}$ Bond 277 (θ_{277})	$2C_{278}$ Bond 278 (θ_{278})	$2C_{279}$ Bond 279 (θ_{279})	$2C_{280}$ Bond 280 (θ_{280})	$2C_{281}$ Bond 281 (θ_{281})	$2C_{282}$ Bond 282 (θ_{282})	$2C_{283}$ Bond 283 (θ_{283})	$2C_{284}$ Bond 284 (θ_{284})	$2C_{285}$ Bond 285 (θ_{285})	$2C_{286}$ Bond 286 (θ_{286})	$2C_{287}$ Bond 287 (θ_{287})	$2C_{288}$ Bond 288 (θ_{288})	$2C_{289}$ Bond 289 (θ_{289})	$2C_{290}$ Bond 290 (θ_{290})	$2C_{291}$ Bond 291 (θ_{291})	$2C_{292}$ Bond 292 (θ_{292})	$2C_{293}$ Bond 293 (θ_{293})	$2C_{294}$ Bond 294 (θ_{294})	$2C_{295}$ Bond 295 (θ_{295})	$2C_{296}$ Bond 296 (θ_{296})	$2C_{297}$ Bond 297 (θ_{297})	$2C_{298}$ Bond 298 (θ_{298})	$2C_{299}$ Bond 299 (θ_{299})	$2C_{300}$ Bond 300 (θ_{300})	$2C_{301}$ Bond 301 (θ_{301})	$2C_{302}$ Bond 302 (θ_{3
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SULFIDES ($C_nH_{2n+2}S_m$, $n = 2, 3, 4, 5 \dots \infty$)

The alkyl sulfides, $C_nH_{2n+2}S_m$, comprise two types of $C-S$ functional groups, one for t-butyl groups corresponding to the C and the other for the remaining general alkyl groups including methyl. The alkyl portion of the alkyl sulfide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfides are equivalent to those in branched-chain alkanes.

Each $C-S$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the S AO to form a MO permits each participating orbital to decrease in radius and energy. Since the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243), c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. As in the case of thiols, C_2 of Eq. (15.52) for the $C-S$ -bond MO given by Eq. (15.127) is $C_2(C2sp^3HO \text{ to } S) = 0.64965$.

The $C-S$ group of alkyl sulfides is equivalent to that of thiols where $E_r(atom-atom,msp^3AO)$ is -0.72457 eV (Eq. (14.151)). The t-butyl- $C-S$ group is also equivalent to that of thiols except that the energy parameters corresponding to the oscillation in the transition state are matched to those of the t-butyl group.

The symbols of the functional groups of branched-chain alkyl sulfides are given in Table 15.153. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfides are given in Tables 15.154, 15.155, and 15.156, respectively. Consider that the $C-S$ bond is along the x axis in the xy -plane. The S nucleus is at the focus $+c$ and the C nucleus is at the focus $-c$. The elliptic angle θ' is taken as counterclockwise from the x -axis for S and as clockwise from the $-x$ -axis for C . The total energy of each alkyl sulfide given in Table 15.157 was calculated as the sum

over the integer multiple of each $E_D(\text{Group})$ of Table 15.156 corresponding to functional-group composition of the molecule. E_{mg} given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of alkyl sulfides determined using Eqs. (15.79-15.108) are given in Table 15.158.

Table 15.153. The symbols of functional groups of alkyl sulfides.

Functional Group	Group Symbol
C-S (methyl, alkyl)	C-S (i)
C-S ((CH ₃), C-S-)	C-S (ii)
CH ₃ group	C-H (CH ₃)
CH ₃ group	C-H (CH ₃)
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (tert to tert-C)	C-C (e)
CC (tert to iso-C)	C-C (f)

Table 15.154. The geometrical bond parameters of alkyl sulfides and experimental values [1].

Parameter	C-S (i) Group	C-S (ii) Group	C-H (CH ₃) Group	C-H (CH ₃) Group	C-H (CH ₃) Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
σ (Å)	1.90975	1.90975	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
σ' (Å)	1.71455	1.71455	1.04856	1.05553	1.03661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2\sigma'$ (Å)	1.81460	1.81460	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.807 (dimethyl sulfide)	1.807 (dimethyl sulfide)	1.107 (C-H propane)	1.107 (C-H propane)	1.122 (isobutane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)
	1.813 (ethyl methyl sulfide, avg.)	1.813 (ethyl methyl sulfide, avg.)	1.117 (C-H butane)	1.117 (C-H butane)		1.531 (butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)
b, c (Å)	0.84112	0.84112	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
c	0.89778	0.89778	0.63380	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.155. The MO to HO intercept geometrical bond parameters of alkyl sulfides. R, R', R'' are H or alkyl groups. E_p is $E_p(\text{atom} - \text{atom}, \text{group}, \text{AO})$.

Bond	Atom	E_p (eV) Bond 1	E_p (eV) Bond 2	E_p (eV) Bond 3	E_p (eV) Bond 4	Final Total Energy C2sp ² (eV)	r_{bond} (a_0)	E_{bond} (eV) Final	$E(\text{C2sp}^2)$ (eV) Final	θ' (°)	θ (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$R-S-R$ (C-S (I) and (II))	S	-0.34229	-0.34229	0	0		1.32010	-15.5033		120.96	90.04	52.88	1.15202	0.56103
$H_3C-S-C_6H_5$	C	-0.34229	0	0	0	-151.97798	0.91771	-15.18004	-14.99117	120.79	49.21	53.75	1.12937	0.58518
$H_3C-S-C_6H_5$	C	-0.34229	-0.92918	0	0	-152.90716	0.91771	-16.11722	-15.92536	121.09	51.31	51.57	1.18689	0.52765
$H_3C-S-C(CH_3)_3$ (C-S (I) and (II))	C	-0.34229	-0.72457	-0.72457	-0.72457	-154.13170	0.91771	-17.36176	-17.17090	123.97	54.03	48.94	1.25430	0.60025
C-H (CH ₃)	C	-0.92918	0	0	0	-152.54487	0.91771	-15.7493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
C-H (CH ₃)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.68412	-16.49325	68.47	111.53	35.84	1.34466	0.29933
$H_3C-S-C_6H_5$ (C-C (a))	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	-17.61330	-17.42344	61.10	118.90	31.37	1.42988	0.37326
$H_3C-S-C_6H_5$ (C-C (b))	C	-0.92918	0	0	0	-152.54487	0.91771	-15.7493	-15.56407	63.82	116.18	30.08	1.33879	0.38106
$R-H_3C-S-C_6H_5$ (C-C (c))	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.68412	-16.49325	56.41	123.59	26.06	1.50890	0.45117
$R-H_3C-S-C_6H_5$ (C-C (d))	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	-17.61330	-17.42344	48.30	131.70	21.90	1.97162	0.51388
$\text{un}^{\text{un}}[R-H_3C-S-C_6H_5]$ (C-C (e))	C	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	-17.93866	-17.73779	48.21	131.79	21.74	1.95754	0.50370
$\text{un}^{\text{un}}[R-H_3C-S-C_6H_5]$ (C-C (f))	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	-17.61330	-17.42344	48.30	131.70	21.90	1.97162	0.51388
$\text{un}^{\text{un}}[R-H_3C-S-C_6H_5]$ (C-C (g))	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.51999	0.91771	-17.93866	-17.73779	50.04	129.96	22.66	1.94462	0.49398
$\text{un}^{\text{un}}[R-H_3C-S-C_6H_5]$ (C-C (h))	C	-0.72457	-0.92918	-0.92918	0	-154.18663	0.91771	-17.40869	-17.21783	32.78	122.22	24.04	1.99443	0.47219
$\text{un}^{\text{un}}[R-H_3C-S-C_6H_5]$ (C-C (i))	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.51999	0.91771	-17.93866	-17.73779	50.04	129.96	22.66	1.94462	0.49398

Table 15.156. The energy parameters (eV) of functional groups of alkyl sulfides.

[illegible]

Table 15.157. The total bond energies of alkyl sulfides calculated using the functional group composition and the energies of Table 15.156 compared to the experimental values [3]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_{T(i=exp)}$ (eV) values based on composition is given by (15.58).

Formula	Name	C-S (i)	C-S (ii)	CH ₃	CH ₂	CH	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₂ H ₆ S	Dimethyl sulfide	2	0	2	0	0	0	0	0	0	0	0	0	31.67664	31.672	0.00048
C ₃ H ₈ S	Ethyl methyl sulfide	1	0	2	1	0	0	0	0	0	0	0	0	43.81438	43.848	0.00078
C ₄ H ₁₀ S	Diethyl sulfide	2	0	2	2	0	0	0	0	0	0	0	0	55.97208	56.043	0.00125
C ₅ H ₁₂ S	Methyl propyl sulfide	2	0	2	2	0	0	0	0	0	0	0	0	55.97208	56.029	0.00102
C ₆ H ₁₄ S	Isopropyl methyl sulfide	2	0	3	0	1	0	2	0	0	0	0	0	56.07297	56.115	0.00075
C ₆ H ₁₄ S	Butyl methyl sulfide	2	0	2	3	0	0	0	0	0	0	0	0	68.12978	68.185	0.00081
C ₆ H ₁₄ S	n-Butyl methyl sulfide	1	1	4	0	0	0	0	3	0	0	0	-1	68.23245	68.281	0.00144
C ₆ H ₁₄ S	Ethyl propyl sulfide	2	0	2	3	0	0	0	0	0	0	0	0	68.12978	68.210	0.00117
C ₆ H ₁₄ S	Ethyl isopropyl sulfide	2	0	3	2	1	0	2	0	0	0	0	0	68.23067	68.250	0.00174
C ₆ H ₁₄ S	Diisopropyl sulfide	2	0	4	0	2	0	0	0	0	0	0	0	80.49748	80.542	0.00065
C ₆ H ₁₄ S	Butyl ethyl sulfide	2	0	2	4	0	0	0	0	0	0	0	0	80.28748	80.332	0.00132
C ₆ H ₁₄ S	Diethyl sulfide	2	0	2	4	0	0	0	0	0	0	0	0	80.28748	80.332	0.00132
C ₆ H ₁₄ S	Methyl pentyl sulfide	2	0	2	4	0	0	0	0	0	0	0	0	104.60788	104.701	0.00096
C ₆ H ₁₄ S	Di-sec-butyl sulfide	2	0	2	6	0	0	0	0	0	0	0	0	104.60788	104.701	0.00096
C ₆ H ₁₄ S	Di-tert-butyl sulfide	2	0	4	2	2	2	4	0	0	0	0	-2	104.90132	104.920	0.00011
C ₆ H ₁₄ S	Di-sec-butyl sulfide	0	2	6	0	0	0	0	6	0	0	0	0	104.90132	104.920	0.00011
C ₆ H ₁₄ S	Dipentyl sulfide	2	0	4	2	2	0	0	0	0	0	0	0	104.74800	104.834	0.00082
C ₆ H ₁₄ S	Dipentyl sulfide	2	0	4	2	2	0	0	0	0	0	0	0	128.91828	128.979	0.00047
C ₆ H ₁₄ S	Diisopentyl sulfide	2	0	4	4	2	2	6	0	0	0	0	0	129.66340	129.151	0.00068

Table 15.158. The bond angle parameters of alkyl sulfides and experimental values [1]. In the calculation of θ_s , the parameters from the preceding angle were used. E_r is $E_r(\text{atom-atom, msp}^3 \text{AO})$.

Bond Angle	$2c'$ Bond 1 (θ_s)	$2c'$ Bond 2 (θ_s)	$2c'$ Torsional Angle (θ_s)	E_r (kcal/mole) Atom 1	Atom 1 Hybridization Designation (Table 15.1A)	E_r (kcal/mole) Atom 2	Atom 2 Hybridization Designation (Table 15.1A)	c_1 Atom 1	c_2 Atom 2	c_3	c_4	E_r (eV)	θ_s ($^\circ$)	θ_1 ($^\circ$)	θ_2 ($^\circ$)	Cal. θ ($^\circ$)	Exp. θ ($^\circ$)
$\angle C_1 S C_2$ (C-S-C)	3.42910	3.42910	5.2173	-16.11722	11	-16.11722	11	0.84418	0.84418	1	1	-1.83536	99.06			99.06	99.05 (dimethyl sulfide)
$\angle C_1 S C_2$ (C-S-C)	3.42910	3.42910	5.1381	-15.75493 methyl C_s	7	-16.68412	25	0.86359	0.81549	1	1	-1.83536	97.04			97.04	97 (ethyl methyl sulfide)
$\angle C_1 S C_2$ (C-S-C)	3.42910	2.91547	5.3364	-10.36001	S	-16.27490	15	0.6985 (eq. 15.127)	0.83500	1	0.64965 (eq. 15.127)	-0.72457	114.27			114.27	114.0 (ethyl methyl sulfide)
Methyl $\angle H C_1 S H$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	0.75	0	108.44			108.44	107 (propane)
$\angle C_1 C_2 C_3$													69.51			110.49	111.0 (propane) 113.8 (butane) 110.8 (propane)
$\angle C_1 C_2 H$													69.51			110.49	111.0 (propane) 113.8 (butane) 110.8 (propane)
Methyl $\angle H C_1 C_2 H$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	0.75	0	108.44			108.44	107 (propane)
$\angle C_1 C_2 C_3$																109.30	109.3 (dimethyl sulfide)
$\angle C_1 C_2 H$																109.30	109.3 (dimethyl sulfide)
$\angle C_1 C_2 C_3$	2.91547	2.91547	4.7958	-16.68412	25	-16.68412	25	0.81549	0.81549	1	1	-1.83535	110.57			110.57	110.8 (isobutane)
$\angle C_1 C_2 H$																110.57	110.8 (isobutane)
$\angle C_1 C_2 C_3$	2.91547	2.11332	4.1633	-15.55033 C_s	S	-14.82575 C_s	1	0.87495	0.91771	0.75	1	0	110.76			110.76	
$\angle C_1 C_2 H$																110.76	
$\angle C_1 C_2 C_3$	2.91547	2.09711	4.1633	-15.55033 C_s	S	-14.82575 C_s	1	0.87495	0.91771	0.75	1	0	111.27			111.27	111.4 (isobutane)
$\angle C_1 C_2 C_3$	2.90327	2.90327	4.7958	-15.55033 C_s	S	-14.82575 C_s	1	0.87495	0.91771	0.75	1	-1.83836	111.27			111.27	111.4 (isobutane)
$\angle C_1 C_2 C_3$													72.50			107.50	

DISULFIDES ($C_nH_{2n+2}S_{2m}$, $n=2,3,4,5,\dots,\infty$)

The alkyl disulfides, $C_nH_{2n+2}S_{2m}$, comprise C-S and S-S functional groups. The alkyl portion of the alkyl disulfide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in disulfides are equivalent to those in branched-chain alkanes.

Each C-S group is equivalent to that of general alkyl sulfides given in the corresponding section. As in the case of thiols and sulfoxides, C_2 of Eq. (15.52) for the C-S bond MO given by Eq. (15.127) is $C_2(C2sp^3HO \text{ to } S) = 0.64965$ and $E_r(atom - atom, msp^3.AO)$ is -0.72457 eV (Eq. (14.151)).

The S-S group is solved as an H_2 -type-ellipsoidal-MO that is energy matched to the energy of sulfur, $E(S) = -10.36001 \text{ eV}$, such that $E(AO / HO) = -10.36001 \text{ eV}$ in Eq. (15.42) with $E_r(AO / HO) = E(AO / HO)$. The S-S-bond MO is further energy matched to the $C2sp^3$ HO of the C-S-bond MO. C_2 of Eq. (15.52) for the S-S-bond MO given by Eq. (15.127) is also $C_2(C2sp^3HO \text{ to } S) = 0.64965$. In order to match $E_r(atom - atom, msp^3.AO)$ of the C-S group (-0.72457 eV (Eq. (14.151))), $E_r(atom - atom, msp^3.AO)$ of the S-S-bond MO is determined using a linear combination of the AOs corresponding to -0.72457 eV and 0 eV in Eq. (15.29), Eq. (15.31), and Eqs. (15.19-15.20). The result corresponding to bond order 1/2I in Table 15.2 is $E_r(atom - atom, msp^3.AO) = -0.36229 \text{ eV}$.

The symbols of the functional groups of branched-chain alkyl disulfides are given in Table 15.159. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl disulfides are given in Tables 15.160, 15.161, and 15.162, respectively. The total energy of each alkyl disulfide given

in Table 15.163 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.162 corresponding to functional-group composition of the molecule. E_{mag} given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of alkyl disulfides determined using Eqs. (15.79-15.108) are given in Table 15.164.

Table 15.159. The symbols of functional groups of alkyl disulfides.

Functional Group	Group Symbol
C-S	C-S
S-S	S-S
CH ₃ group	C-H (CH ₃)
CH ₂ group	C-H (CH ₂)
CH	C-H
CC bond (n-C)	C-C' (a)
CC bond (iso-C)	C-C' (b)
CC bond (tert-C)	C-C' (c)
CC (iso to iso-C)	C-C' (d)
CC (1 to 1-C)	C-C' (e)
CC (1 to 1-C)	C-C' (f)

Table 15.160. The geometrical bond parameters of alkyl disulfides and experimental values [1]

Parameter	C-S (i) Group	S-S Group	C-H (CH ₃) Group	C-H (CH ₂) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
σ (Å)	1.90975	2.37173	1.64920	1.67122	1.67463	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
σ' (Å)	1.71455	1.91070	1.04856	1.05133	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length 2 σ' (Å)	1.81460	2.02220	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.816 (dimethyl disulfide)	2.029 (dimethyl disulfide)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
b_e (Å)	0.84112	1.40510	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
ϵ	0.89778	0.80562	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 13.161. The MO to HO intercept geometrical bond parameters of allyl disulfides. R, R', R'' are H or alkyl groups. E_p is $E_p(\text{atom} - \text{atom}, \text{resp. } AO)$.

Bond	Atom	E_p (eV) Bond 1	E_p (eV) Bond 2	E_p (eV) Bond 3	E_p (eV) Bond 4	Final Total Energy (eV)	r_{bond} (a_0)	E_{residual} (eV) Final	$E(\sigma_{2p})$ (eV) Final	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
R_5-SR ($C-S$ (I) and (II))	S	-0.34329	-0.18114	0	0	-153.6918	0.81327	-15.4918	-14.9917	94.35	85.75	1.4513	0.6558
$H_2C-S-S-C_2H_5CH_2R$	C	-0.34329	0	0	0	-151.97708	0.91771	-15.18804	-14.9917	100.79	49.21	1.1937	0.5518
$H_2C-S-S-C_2H_5CH_2R$ ($C-S$ (I))	C	-0.34329	-0.92918	0	0	-152.00716	0.91771	-16.11722	-15.92636	124.69	51.31	1.1689	0.5765
$C-H$ (CH_3)	C	-0.34329	-0.72457	-0.72457	-0.72457	-154.13170	0.91771	-17.36176	-17.17690	125.97	54.03	1.2450	0.46025
$C-H$ (CH_2)	C	-0.92918	0	0	0	-152.54487	0.91771	-15.75493	-15.56407	77.49	102.51	1.2354	0.18708
$C-H$ (CH)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.68412	-16.49225	68.47	111.53	1.3346	0.18933
$H_2C-C_2H_5CH_2-$ ($C-C$ (I))	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	-17.61330	-17.42244	61.10	118.90	1.4298	0.37226
$H_2C-C_2H_5CH_2-$ ($C-C$ (II))	C	-0.92918	0	0	0	-152.54487	0.91771	-15.75493	-15.56407	63.82	116.18	1.3379	0.38106
$R-H_2C-C_2H_5CH_2-$ ($C-C$ (I))	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.68412	-16.49225	56.41	123.59	1.5080	0.45117
$R-H_2C-C_2H_5CH_2-$ ($C-C$ (II))	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	-17.61330	-17.42244	48.30	131.70	1.5712	0.51288
$R-H_2C-C_2H_5CH_2-$ ($C-C$ (III))	C	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	-17.92666	-17.73779	44.21	131.79	1.9574	0.50570
$R-H_2C-C_2H_5CH_2-$ ($C-C$ (IV))	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	-17.61330	-17.42244	48.30	131.70	1.9712	0.51348
$R-H_2C-C_2H_5CH_2-$ ($C-C$ (V))	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	-17.92866	-17.73779	50.04	129.96	1.9462	0.49208
$R-H_2C-C_2H_5CH_2-$ ($C-C$ (VI))	C	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	-17.40869	-17.21783	52.78	131.22	1.9743	0.47279
$R-H_2C-C_2H_5CH_2-$ ($C-C$ (VII))	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	-17.92866	-17.73779	50.04	129.96	1.9462	0.49208

Table 15.162. The energy parameters (eV) of functional groups of allyl disulfides.

Parameters	C-S (f) Group	C-S (g) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
η_1	1	1	3	1	1	1	1	1	1
η_2	0	0	2	1	0	0	0	0	0
η_3	0	0	0	0	0	0	0	0	0
η_4	0	0	0	0	0	0	0	0	0
η_5	0.5	0.5	0.75	0.75	0.5	0.5	0.5	0.5	0.5
η_6	0.64965	0.64965	1	1	1	1	1	1	1
η_7	1	1	1	1	1	1	1	1	1
η_8	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_9	0	0	0	0	0	0	0	0	0
η_{10}	2	2	1	2	2	2	2	2	2
η_{11}	0	0	3	1	0	0	0	0	0
η_{12}	0.5	0.5	0.75	0.75	0.5	0.5	0.5	0.5	0.5
η_{13}	0.64965	0.64965	1	1	1	1	1	1	1
η_{14}	1	1	1	1	1	1	1	1	1
η_{15}	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{16}	0	0	0	0	0	0	0	0	0
η_{17}	2	2	1	2	2	2	2	2	2
η_{18}	0	0	3	1	0	0	0	0	0
η_{19}	0.5	0.5	0.75	0.75	0.5	0.5	0.5	0.5	0.5
η_{20}	0.64965	0.64965	1	1	1	1	1	1	1
η_{21}	1	1	1	1	1	1	1	1	1
η_{22}	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{23}	0	0	0	0	0	0	0	0	0
η_{24}	2	2	1	2	2	2	2	2	2
η_{25}	0	0	3	1	0	0	0	0	0
η_{26}	0.5	0.5	0.75	0.75	0.5	0.5	0.5	0.5	0.5
η_{27}	0.64965	0.64965	1	1	1	1	1	1	1
η_{28}	1	1	1	1	1	1	1	1	1
η_{29}	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{30}	0	0	0	0	0	0	0	0	0
η_{31}	2	2	1	2	2	2	2	2	2
η_{32}	0	0	3	1	0	0	0	0	0
η_{33}	0.5	0.5	0.75	0.75	0.5	0.5	0.5	0.5	0.5
η_{34}	0.64965	0.64965	1	1	1	1	1	1	1
η_{35}	1	1	1	1	1	1	1	1	1
η_{36}	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{37}	0	0	0	0	0	0	0	0	0
η_{38}	2	2	1	2	2	2	2	2	2
η_{39}	0	0	3	1	0	0	0	0	0
η_{40}	0.5	0.5	0.75	0.75	0.5	0.5	0.5	0.5	0.5
η_{41}	0.64965	0.64965	1	1	1	1	1	1	1
η_{42}	1	1	1	1	1	1	1	1	1
η_{43}	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{44}	0	0	0	0	0	0	0	0	0
η_{45}	2	2	1	2	2	2	2	2	2
η_{46}	0	0	3	1	0	0	0	0	0
η_{47}	0.5	0.5	0.75	0.75	0.5	0.5	0.5	0.5	0.5
η_{48}	0.64965	0.64965	1	1	1	1	1	1	1
η_{49}	1	1	1	1	1	1	1	1	1
η_{50}	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{51}	0	0	0	0	0	0	0	0	0
η_{52}	2	2	1	2	2	2	2	2	2
η_{53}	0	0	3	1	0	0	0	0	0
η_{54}	0.5	0.5	0.75	0.75	0.5	0.5	0.5	0.5	0.5
η_{55}	0.64965	0.64965	1	1	1	1	1	1	1
η_{56}	1	1	1	1	1	1	1	1	1
η_{57}	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{58}	0	0	0	0	0	0	0	0	0
η_{59}	2	2	1	2	2	2	2	2	2
η_{60}	0	0	3	1	0	0	0	0	0
η_{61}	0.5	0.5	0.75	0.75	0.5	0.5	0.5	0.5	0.5
η_{62}	0.64965	0.64965	1	1	1	1	1	1	1
η_{63}	1	1	1	1	1	1	1	1	1
η_{64}	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{65}	0	0	0	0	0	0	0	0	0
η_{66}	2	2	1	2	2	2	2	2	2
η_{67}	0	0	3	1	0	0	0	0	0
η_{68}	0.5	0.5	0.75	0.75	0.5	0.5	0.5	0.5	0.5
η_{69}	0.64965	0.64965	1	1	1	1	1	1	1
η_{70}	1	1	1	1	1	1	1	1	1
η_{71}	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{72}	0	0	0	0	0	0	0	0	0
η_{73}	2	2	1	2	2	2	2	2	2
η_{74}	0	0	3	1	0	0	0	0	0
η_{75}	0.5	0.5	0.75	0.75	0.5	0.5	0.5	0.5	0.5
η_{76}	0.64965	0.64965	1	1	1	1	1	1	1
η_{77}	1	1	1	1	1	1	1	1	1
η_{78}	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{79}	0	0	0	0	0	0	0	0	0
η_{80}	2	2	1	2	2	2	2	2	2
η_{81}	0	0	3	1	0	0	0	0	0
η_{82}	0.5	0.5	0.75	0.75	0.5	0.5	0.5	0.5	0.5
η_{83}	0.64965	0.64965	1	1	1	1	1	1	1
η_{84}	1	1	1	1	1	1	1	1	1
η_{85}	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{86}	0	0	0	0	0	0	0	0	0
η_{87}	2	2	1	2	2	2	2	2	2
η_{88}	0	0	3	1	0	0	0	0	0
η_{89}	0.5	0.5	0.75	0.75	0.5	0.5	0.5	0.5	0.5
η_{90}	0.64965	0.64965	1	1	1	1	1	1	1
η_{91}	1	1	1	1	1	1	1	1	1
η_{92}	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{93}	0	0	0	0	0	0	0	0	0
η_{94}	2	2	1	2	2	2	2	2	2
η_{95}	0	0	3	1	0	0	0	0	0
η_{96}	0.5	0.5	0.75	0.75	0.5	0.5	0.5	0.5	0.5
η_{97}	0.64965	0.64965	1	1	1	1	1	1	1
η_{98}	1	1	1	1	1	1	1	1	1
η_{99}	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{100}	0	0	0	0	0	0	0	0	0

Table 15.163. The total bond energies of allyl disulfides calculated using the functional group composition and the energies of Table 15.162 compared to the experimental values [3]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_{f, group}$ (eV) values based on composition is given by (15.58).

Formula	Name	C-S Group	S-S Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_4H_8S_2$	Directly disulfide	2	1	0	0	0	0	0	0	0	0	34.413	34.413	-0.00199
$C_4H_6S_2$	Disubstituted disulfide	2	1	2	2	0	0	0	0	0	0	58.79667	58.873	0.00120
$C_4H_4S_2$	Disubstituted disulfide	2	1	4	4	0	0	0	0	0	0	83.1207	83.169	0.00068
$C_4H_2S_2$	Disubstituted disulfide	2	1	6	6	0	0	0	0	0	-2	107.9653	107.919	-0.00072

SULFOXIDES ($C_nH_{2n+2}(SO)_m$, $n = 2, 3, 4, 5, \dots, \infty$)

The alkyl sulfoxides, $C_nH_{2n+2}(SO)_m$, comprise a $C-SO-C$ moiety that comprises $C-S$ and SO functional groups. The alkyl portion of the alkyl sulfoxide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfoxides are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^2 2s^2 2p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state 3P_2 . The SO functional group comprises a double bond between the two unpaired electrons of O . The sulfur atom is energy matched to the $C2sp^3$ HO. In alkyl sulfoxides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C, 2sp^3) = -14.63489 \text{ eV}$ (Eq. (15.25)), and the S AO has an initial energy of $E(S) = -10.36001 \text{ eV}$ [38]. To meet the equipotential condition of the union of the $S=O$ H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $S=O$ -bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(O \text{ to } S3sp^3 \text{ to } C2sp^3 HO) &= \frac{E(O)}{E(S)} c_2(C2sp^3 HO) \\ &= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}} (0.91771) \\ &= 1.20632 \end{aligned} \quad (15.128)$$

The S atom also forms a single bond with each of the $C2sp^3$ HOs of the two $C-S$ groups. The formation of these bonds is permitted by the hybridization of the four electrons of the $S3p$ shell to give the orbital arrangement:

$$\begin{array}{cccc} & \text{3sp}^3 \text{ state} & & \\ \uparrow & \uparrow & \uparrow & \uparrow \\ 0,0 & 1,-1 & 1,0 & 1,1 \end{array} \quad (15.129)$$

where the quantum numbers (ℓ, m_ℓ) are below each electron. The $3s$ shell remains unchanged. Then, the Coulombic energy $E_{Coulomb}(S, 3sp^3)$ of the outer electron of the $S3sp^3$ shell given by Eq. (15.118) with $r_{3sp^3} = 1.17585a_0$ (Eq. (15.119)) is -11.57099 eV . Using Eq. (15.16) with the radius of the sulfur atom $r_{16} = 1.32010a_0$ given by Eq. (10.341), the energy $E(S3sp^3)$ of the 5 outer electron of the $S3sp^3$ shell is given by the sum of $E_{Coulomb}(S3sp^3)$ and $E(magnetic)$:

$$\begin{aligned} E(S3sp^3) &= \frac{-e^2}{8\pi\epsilon_0 r_{3sp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r_{16}^3} \\ &= \frac{-e^2}{8\pi\epsilon_0 1.17585a_0} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (1.32010a_0)^3} \\ &= -11.57099 \text{ eV} + 0.04973 \\ &= -11.52126 \text{ eV} \end{aligned} \quad (15.130)$$

Then, the hybridization energy $E_{hybridization}(S3sp^3)$ of the $S3sp^3$ HO is

$$\begin{aligned} E_{hybridization}(S3sp^3) &= E(S3sp^3) - E(S) \\ &= -11.52126 \text{ eV} - 10.36001 \text{ eV} \\ &= -1.16125 \text{ eV} \end{aligned} \quad (15.131)$$

The SO group is matched to the $C-S$ group with which it shares the common 10 hybridized S atom. Consequently, $E_{hybridization}(S3sp^3)$ is subtracted from $E_T(Group)$ in the determination of $E_D(Group)$ (Eq. 15.56). Furthermore, the energy of the $S=O$ -bond MO is the sum of the component energies of the H_2 -type ellipsoidal MO given in Eq. (15.42) with the energy matched to the final energy of the hybridized S atom such that $E(AO/HO) = E(S3sp^3) = -11.52126 \text{ eV}$ and

$$15 \quad \Delta E_{H_2MO}(AO/HO) = E_{hybridization}(S3sp^3) = -1.16125 \text{ eV}. \quad \text{Then,}$$

$E_T(AO/HO) = E(S) = -10.36001 \text{ eV}$. Also, $E_T(atom-atom, msp^3.AO)$ of the $S=O$ bond is zero since there are no bonds with a $C2sp^3$ HO.

The $C-S$ group is solved as an energy minimum by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell and by hybridizing the four $S3p$ electrons to form a 20 $S3sp^3$ shell, and the sharing of electrons between the $C2sp^3$ HO and the $S3sp^3$ HO to form a MO permits each participating orbital to decrease in radius and energy. Using the Coulombic

energy of the $S3sp^3$ shell, $E_{Coulomb}(S3sp^3)$ given by Eq. (15.120) in Eq. (15.63), the $S3sp^3$ -shell hybridization factor, $c_2(S3sp^3)$, is

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099 \text{ eV}}{-13.60580 \text{ eV}} = 0.85045 \quad (15.132)$$

As in the case of thiols, sulfides, and disulfides, the energy of sulfur is less than the
5 Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_1 and c_2 are equal to one in Eq. (15.52), and the energy matching condition is determined by the C_2 parameter. In alkyl sulfoxides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C, 2sp^3) = -14.63489 \text{ eV}$ (Eq. (15.25)) and the $S3sp^3$ HO has an energy of $E(S3sp^3) = -11.52126 \text{ eV}$ (Eq. (15.130)). To meet the
10 equipotential condition of the union of the $C-S$ H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.52) for the $C-S$ -bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3HO \text{ to } S3sp^3) = \frac{E(S3sp^3)}{E(C, 2sp^3)} c_2(S3sp^3) = \frac{-11.52126 \text{ eV}}{-14.63489 \text{ eV}} (0.85045) = 0.66951 \quad (15.133)$$

As in the case of thiols, sulfides, and disulfides, with the energy of S matched to the
15 Coulombic energy between the electron and proton of H , the energy of the $C-S$ -bond MO is the sum of the component energies of the H_2 -type ellipsoidal MO given in Eq. (15.42) with $E(AO/HO) = 0$ and $E_T(AO/HO) = \Delta E_{H_2MO}(AO/HO)$. For sulfoxides, $\Delta E_{H_2MO}(AO/HO) = -0.72457 \text{ eV}$. Further equivalently, $E_T(atom - atom, msp^3 AO) = -0.72457 \text{ eV}$ (Eq. (14.151)).

20 The symbols of the functional groups of branched-chain alkyl sulfoxides are given in Table 15.165. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfoxides are given in Tables 15.166, 15.167, and 15.168, respectively. Consider that the $C-S$ bond is along the x axis in the xy -plane. The S nucleus is at the focus $+c$ and the C nucleus is at the focus $-c$. The
25 elliptic angle θ' is taken as counterclockwise from the x -axis for S and as clockwise from the $-x$ -axis for C . The total energy of each alkyl sulfoxide given in Table 15.169 was calculated as the sum over the integer multiple of each $E_D(Grup)$ of Table 15.168 corresponding to functional-

group composition of the molecule. The bond angle parameters of alkyl sulfoxides determined using Eqs. (15.79-15.108) are given in Table 15.170.

Table 15.165. The symbols of functional groups of alkyl sulfoxides.

Functional Group	Group Symbol
C-S	$C-S$
SO	SO
CH ₃ group	$C-H (CH_3)$
CH ₂ group	$C-H (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C (a)$
CC bond (iso-C)	$C-C (b)$
CC bond (tert-C)	$C-C (c)$
CC (iso to iso-C)	$C-C (d)$
CC (t to t-C)	$C-C (e)$
CC (t to iso-C)	$C-C (f)$

Table 15.166. The geometrical bond parameters of alkyl sulfoxides and experimental values [1].

Parameter	C-S Group	SO Group	C-H (CH ₃) Group	C-H (CH ₂) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
σ (Å)	1.87525	1.98517	1.67122	1.67465	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
σ' (Å)	1.67271	1.40896	1.04856	1.05661	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length 2 σ' (Å)	1.77031	1.49118	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.799 (dimethyl sulfoxide)	1.485 (dimethyl sulfoxide)	1.107 (C-H propane)	1.117 (C-H propane)	1.122 (isobutane)	1.532 (propane)	1.532 (propane)	1.531 (butane)	1.532 (propane)	1.531 (butane)	1.532 (propane)
Δ_c (Å)	0.84328	1.39847	1.27295	1.29369	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
σ	0.89254	0.70974	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.167. The MO to HQ intercept geometrical bond parameters of alkyl sulfoxides. R, R', R'' are H or alkyl groups. E_p is $E_p(\text{atom} - \text{atom}, \text{aug}^2, 40)$.

Bond	Atom	E_p (eV) Bond 1	E_p (eV) Bond 2	E_p (eV) Bond 3	E_p (eV) Bond 4	Final Total Energy C_{2p}^{Total} (eV)	r_{bond} (a_0)	E_{bond} (eV) Final	$E(C_{2p})$ (eV) Final	θ' ($^\circ$)	θ_1 ($^\circ$)	θ_2 ($^\circ$)	d_1 (a_0)	d_2 (a_0)
$R_2S=O$	S	0	-0.36229	-0.36229	0	1.32010	0.72493	-15.33033	79.78	100.22	39.00	1.54425	0.15529	
$R_2S=O$	O	0	0	0	0	1.00000	0.91771	-18.82575	84.06	95.94	40.75	1.50400	0.09504	
$R_2S=O$	S	-0.36229	-0.36229	0	0	1.32010	0.72493	-15.33033	129.35	50.65	53.56	1.17799	0.55472	
$H_3C-S(O)-C_2H_5$	C	-0.36229	0	0	0	-151.97758	0.91771	-15.18804	-14.99717	130.19	49.81	54.24	1.09461	0.37809
$H_3C-S(O)-C_2H_5$	C	-0.36229	-0.92018	0	0	-155.00716	0.91771	-16.11722	-15.92636	128.05	51.95	52.03	1.15245	0.53026
$C-H(CH_3)$	C	-0.92018	0	0	0	-152.54447	0.91771	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H(CH_3)$	C	-0.92018	-0.92018	0	0	-153.47406	0.91771	-16.64412	-16.49323	88.47	111.53	33.84	1.35495	0.29293
$C-H(CH_3)$	C	-0.92018	-0.92018	-0.92018	0	-154.40324	0.91771	-17.61330	-17.42344	61.10	118.90	31.37	1.42088	0.37326
$H_3C-C_2H_5$	C	-0.92018	0	0	0	-152.54447	0.91771	-15.75493	-15.56407	63.82	116.18	30.01	1.33379	0.38106
$C-C(CH_3)$	C	-0.92018	-0.92018	0	0	-153.47406	0.91771	-16.64412	-16.49323	56.41	123.59	26.06	1.50890	0.45117
$R-H_2C-C_2H_5$	C	-0.92018	-0.92018	-0.92018	0	-154.40324	0.91771	-17.61330	-17.42344	48.30	131.20	21.90	1.59162	0.51388
$C-C(CH_3)$	C	-0.92018	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	-17.92866	-17.73779	48.21	131.79	21.74	1.59754	0.50570
$H_3C-C_2H_5$	C	-0.92018	-0.92018	-0.92018	0	-154.40324	0.91771	-17.61330	-17.42344	48.30	131.70	21.90	1.59162	0.51388
$H_3C-C_2H_5$	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.31399	0.91771	-17.92866	-17.73779	30.04	129.56	22.66	1.94462	0.49208
$H_3C-C_2H_5$	C	-0.72457	-0.92018	-0.92018	0	-154.19863	0.91771	-17.40669	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$C-C(CH_3)$	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	-17.92866	-17.73779	30.04	129.56	22.66	1.94462	0.49208

Table 15.168. The energy parameters (eV) of functional groups of alkyl sulfonides.

Parameters	C-S Group	SO Group	CH ₃ Group	CH ₂ Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
η_1	1	2	3	1	0	1	1	1	1	1	1
η_2	0	0	2	1	0	0	0	0	0	0	0
η_3	0	0	0	0	0	0	0	0	0	0	0
ζ_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
ζ_2	0.66951	1	1	1	1	1	1	1	1	1	1
ζ_3	1	1	1	1	1	1	1	1	1	1	1
ζ_4	1	1.20632	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
ζ_5	0	0	0	0	0	0	0	0	0	0	0
ζ_6	2	4	1	1	1	2	2	2	2	2	2
ζ_7	0	1	3	1	1	0	0	0	0	0	0
ζ_8	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
ζ_9	0.66951	1	1	1	1	1	1	1	1	1	1
ζ_{10}	-46.73032	-87.63003	-107.32778	-70.41425	-35.12015	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214
ζ_{11}	8.13401	19.31315	38.92728	24.78002	12.87680	9.33352	9.33352	9.33352	9.33352	9.33352	9.33352
ζ_{12}	12.47306	20.81183	32.53914	21.06675	10.48382	6.77464	6.77464	6.77464	6.77464	6.77464	6.77464
ζ_{13}	-4.25653	-10.40592	-16.26957	-10.53137	-5.24291	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732
ζ_{14}	0	-11.52126	-15.36407	-15.36407	-14.65489	-15.36407	-15.36407	-15.36407	-15.36407	-15.36407	-15.36407
ζ_{15}	-0.72457	-1.16125	0	0	0	0	0	0	0	0	0
ζ_{16}	0.72457	-10.36001	-15.36407	-15.36407	-14.65489	-15.36407	-15.36407	-15.36407	-15.36407	-15.36407	-15.36407
ζ_{17}	-31.63521	-63.27088	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537
ζ_{18}	-0.72457	0	0	0	0	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836
ζ_{19}	-32.35994	-63.27074	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373
ζ_{20}	30.8880	17.6762	24.9286	24.2751	24.1759	9.43699	9.43699	9.43699	9.43699	9.43699	9.43699
ζ_{21}	20.33104	11.63476	16.40846	15.97831	15.91299	6.21159	6.21159	6.21159	6.21159	6.21159	6.21159
ζ_{22}	-0.28866	-0.21548	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
ζ_{23}	0.08543	0.12832	0.35532	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.12312	0.12312
ζ_{24}	-0.24595	-0.14932	-0.22757	-0.14502	-0.07200	-0.10559	-0.07256	-0.15924	-0.10359	-0.10260	-0.10260
ζ_{25}	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
ζ_{26}	-32.60589	-63.56937	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732
ζ_{27}	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
ζ_{28}	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
ζ_{29}	3.35611	3.86956	12.49186	7.83016	3.37601	4.32744	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.169. The total bond energies of alkyl sulfonides calculated using the functional group composition and the energies of Table 15.168 compared to the experimental values [2].

Formula	Name	C-S Group	SO Group	CH ₃ Group	CH ₂ Group	CH Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH ₃ SO	Dimethyl sulfide	2	1	2	0	0	0	0	0	0	0	0	35.0450	35.033	-0.00233
CH ₃ SO	Dimethyl sulfide	2	1	2	0	0	0	0	0	0	0	0	59.87900	59.801	0.00015
CH ₃ SO	Dimethyl sulfide	2	1	2	0	0	0	0	0	0	0	0	84.15530	84.204	0.00165

SULFOXIDES ($C_nH_{2n+2}(SO)_n$, $n = 2, 3, 4, 5, \dots, \infty$)

The alkyl sulfoxides, $C_nH_{2n+2}(SO)_n$, comprise a $C-SO-C$ moiety that comprises $C-S$ and SO functional groups. The alkyl portion of the alkyl sulfoxide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n -alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfoxides are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^2 2s^2 2p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state 3P_2 . The SO functional group comprises a double bond between the two unpaired electrons of O . The sulfur atom is energy matched to the $C2sp^3$ HO. In alkyl sulfoxides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C, 2sp^3) = -14.63489 \text{ eV}$ (Eq. (15.25)), and the S AO has an initial energy of $E(S) = -10.36001 \text{ eV}$ [38]. To meet the equipotential condition of the union of the $S=O$ H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $S=O$ bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(O \text{ to } S3sp^3 \text{ to } C2sp^3 HO) &= \frac{E(O)}{E(S)} c_2(C2sp^3 HO) \\ &= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}} (0.91771) \\ &= 1.20632 \end{aligned} \quad (15.128)$$

The S atom also forms a single bond with each of the $C2sp^3$ HOs of the two $C-S$ groups. The formation of these bonds is permitted by the hybridization of the four electrons of the $S3p$ shell to give the orbital arrangement:

$$\begin{array}{cccc} & & 3sp^3 \text{ state} & \\ \uparrow & \uparrow & \uparrow & \uparrow \\ \hline 0,0 & 1,-1 & 1,0 & 1,1 \end{array} \quad (15.129)$$

where the quantum numbers (ℓ, m_ℓ) are below each electron. The $3s$ shell remains unchanged. Then, the Coulombic energy $E_{Coulomb}(S, 3sp^3)$ of the outer electron of the $S3sp^3$ shell given by Eq. (15.118) with $r_{3sp^3} = 1.17585a_0$ (Eq. (15.119)) is -11.57099 eV . Using Eq. (15.16) with the radius of the sulfur atom $r_{16} = 1.32010a_0$ given by Eq. (10.341), the energy $E(S3sp^3)$ of the 5 outer electron of the $S3sp^3$ shell is given by the sum of $E_{Coulomb}(S3sp^3)$ and $E(magnetic)$:

$$\begin{aligned} E(S3sp^3) &= \frac{-e^2}{8\pi\epsilon_0 r_{3sp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r_{16}^3} \\ &= \frac{-e^2}{8\pi\epsilon_0 1.17585a_0} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (1.32010a_0)^3} \\ &= -11.57099 \text{ eV} + 0.04973 \\ &= -11.52126 \text{ eV} \end{aligned} \quad (15.130)$$

Then, the hybridization energy $E_{hybridization}(S3sp^3)$ of the $S3sp^3$ HO is

$$\begin{aligned} E_{hybridization}(S3sp^3) &= E(S3sp^3) - E(S) \\ &= -11.52126 \text{ eV} - 10.36001 \text{ eV} \\ &= -1.16125 \text{ eV} \end{aligned} \quad (15.131)$$

The SO group is matched to the $C-S$ group with which it shares the common hybridized S atom. Consequently, $E_{hybridization}(S3sp^3)$ is subtracted from $E_r(Group)$ in the determination of $E_D(Group)$ (Eq. 15.56). Furthermore, the energy of the $S=O$ -bond MO is the sum of the component energies of the H_2 -type ellipsoidal MO given in Eq. (15.42) with the energy matched to the final energy of the hybridized S atom such that $E(AO/HO) = E(S3sp^3) = -11.52126 \text{ eV}$ and

$$15 \quad \Delta E_{H_2MO}(AO/HO) = E_{hybridization}(S3sp^3) = -1.16125 \text{ eV}. \quad \text{Then,}$$

$E_r(AO/HO) = E(S) = -10.36001 \text{ eV}$. Also, $E_r(atom-atom, msp^3.AO)$ of the $S=O$ bond is zero since there are no bonds with a $C2sp^3$ HO.

The $C-S$ group is solved as an energy minimum by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell and by hybridizing the four $S3p$ electrons to form a $S3sp^3$ shell, and the sharing of electrons between the $C2sp^3$ HO and the $S3sp^3$ HO to form a MO permits each participating orbital to decrease in radius and energy. Using the Coulombic

energy of the $S3sp^3$ shell, $E_{Coulomb}(S3sp^3)$ given by Eq. (15.120) in Eq. (15.63), the $S3sp^3$ -shell hybridization factor, $c_2(S3sp^3)$, is

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099 \text{ eV}}{-13.60580 \text{ eV}} = 0.85045 \quad (15.132)$$

As in the case of thiols, sulfides, and disulfides, the energy of sulfur is less than the
 5 Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_1 and c_2 are equal to one in Eq. (15.52), and the energy matching condition is determined by the C_2 parameter. In alkyl sulfoxides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \text{ eV}$ (Eq. (15.25)) and the $S3sp^3$ HO has an energy of $E(S3sp^3) = -11.52126 \text{ eV}$ (Eq. (15.130)). To meet the
 10 equipotential condition of the union of the $C-S$ H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.52) for the $C-S$ -bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3 \text{ HO to } S3sp^3) = \frac{E(S3sp^3)}{E(C,2sp^3)} c_2(S3sp^3) = \frac{-11.52126 \text{ eV}}{-14.63489 \text{ eV}} (0.85045) = 0.66951 \quad (15.133)$$

As in the case of thiols, sulfides, and disulfides, with the energy of S matched to the
 15 Coulombic energy between the electron and proton of H , the energy of the $C-S$ -bond MO is the sum of the component energies of the H_2 -type ellipsoidal MO given in Eq. (15.42) with

$$E(AO/HO) = 0 \quad \text{and} \quad E_r(AO/HO) = \Delta E_{H_2MO}(AO/HO). \quad \text{For sulfoxides,}$$

$$\Delta E_{H_2MO}(AO/HO) = -0.72457 \text{ eV}.$$

Further equivalently,

$$E_r(\text{atom} - \text{atom}, msp^3 AO) = -0.72457 \text{ eV} \quad (\text{Eq. (14.151)}).$$

20 The symbols of the functional groups of branched-chain alkyl sulfoxides are given in Table 15.165. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfoxides are given in Tables 15.166, 15.167, and 15.168, respectively. Consider that the $C-S$ bond is along the x axis in the xy -plane. The S nucleus is at the focus $+c$ and the C nucleus is at the focus $-c$. The
 25 elliptic angle θ' is taken as counterclockwise from the x -axis for S and as clockwise from the $-x$ -axis for C . The total energy of each alkyl sulfoxide given in Table 15.169 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.168 corresponding to functional-

group composition of the molecule. The bond angle parameters of alkyl sulfoxides determined using Eqs. (15.79-15.108) are given in Table 15.170.

Table 15.165. The symbols of functional groups of alkyl sulfoxides.

Functional Group	Group Symbol
C-S	$C-S$
SO	SO
CH ₃ group	$C-H (CH_3)$
CH ₂ group	$C-H (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C (a)$
CC bond (iso-C)	$C-C (b)$
CC bond (tert-C)	$C-C (c)$
CC (iso to iso-C)	$C-C (d)$
CC (t to t-C)	$C-C (e)$
CC (t to iso-C)	$C-C (f)$

Table 15.166. The geometrical bond parameters of alkyl sulfoxides and experimental values [1].

Parameter	C-S Group	S-O Group	C-H (CH ₃) Group	C-H (CH ₃) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
σ (°)	1.87325	1.98517	1.67122	1.67122	1.67463	1.24999	1.24999	2.10725	2.12499	2.10725	2.10725
τ (°)	1.67271	1.40896	1.05553	1.05553	1.05661	1.43744	1.43744	1.45164	1.45744	1.45164	1.45164
Bond Length 2c (Å)	1.77031	1.49118	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp Bond Length (Å)	1.799 (dimethyl sulfoxide)	1.485 (dimethyl sulfoxide)	1.107 (C-H propane)	1.107 (C-H propane)	1.122 (isobutane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)
θ_1 (°)	0.84328	1.39847	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
θ_2 (°)	0.89294	0.70974	0.63380	0.63135	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.167. The MO to HO intercept geometrical bond parameters of alkyl sulfoxides. R_1, R_2, R' are H or alkyl groups. E_p is $E_p(\text{atom} - \text{atom}, \text{exp}, \text{AO})$.

Bond	Atom	E_p (eV) Bond 1	E_p (eV) Bond 2	E_p (eV) Bond 3	E_p (eV) Bond 4	Final Total Energy C_{exp} (eV)	r_{exp} (Å)	r_{exp} (Å)	E_{exp} (eV) Final	$E(\text{exp})$ (eV) Final	θ (°)	θ_1 (°)	θ_2 (°)	d_1 (Å)	d_2 (Å)
$R_1S=O$	S	0	-0.36239	-0.36239	0	1.32010	0.87465	1.32010	-15.5033	-15.5033	79.78	100.22	34.00	1.56425	0.15539
$R_2S=O$	O	0	0	0	0	1.00600	0.91771	1.00600	-14.82775	-14.82775	84.06	95.04	40.75	1.50406	0.09304
$H_1C_1-S(O)-C_2H_2CH_3R$	S	-0.16229	-0.16229	0	0	1.32010	0.87465	1.32010	-15.5033	-15.5033	120.35	50.63	53.36	1.1789	0.5472
$H_1C_1-S(O)-C_2H_2CH_3R$	C ₁	-0.16229	-0.16229	0	0	-15.19778	0.91771	0.89582	-15.18004	-15.18004	130.19	49.81	54.24	1.09461	0.7809
$C-H (CH_3)$	C	-0.92918	0	0	0	-153.80716	0.91771	0.84418	-16.11722	-16.11722	128.05	51.95	52.08	1.15245	0.50026
$C-H (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.85359	-15.75493	-15.75493	77.49	102.51	41.48	1.23564	0.18708
$C-H (CH)$	C	-0.92918	-0.92918	0	0	-153.17406	0.91771	0.81549	-16.68412	-16.68412	68.47	111.53	35.84	1.35486	0.20033
$H_1C_1C_2H_2CH_3$	C ₂	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.61330	61.10	118.90	31.37	1.42988	0.37326
$H_1C_1C_2H_2CH_3$	C ₁	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.75493	63.82	116.18	30.08	1.33879	0.38105
$(C-C (e))$	C ₁	-0.92918	-0.92918	0	0	-153.17406	0.91771	0.81549	-16.68412	-16.68412	56.41	132.59	26.06	1.98970	0.43117
$R-H_1C_1C_2(H_1C_1-R)HCH_3$	C ₁	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.61330	48.20	131.70	21.90	1.97162	0.51388
$R-H_1C_1C_2(H_1C_1-R)HCH_3$	C ₂	-0.92918	-0.92918	-0.92918	-0.92918	-154.71860	0.91771	0.75819	-17.92866	-17.92866	48.21	131.70	21.74	1.97162	0.50370
$HOHC_1(R-H_1C_1C_2-R)HCH_3$	C ₁	-0.92918	-0.92918	-0.92918	-0.92918	-154.40324	0.91771	0.77247	-17.61330	-17.61330	48.30	131.70	21.90	1.97162	0.51388
$HOHC_1(R-H_1C_1C_2-R)HCH_3$	C ₂	-0.92918	-0.92918	-0.92918	-0.92918	-154.51399	0.91771	0.76763	-17.92866	-17.92866	50.04	129.96	22.66	1.94462	0.49298
$HOHC_1(R-H_1C_1C_2-R)HCH_3$	C ₁	-0.92918	-0.92918	-0.92918	0	-154.15963	0.91771	0.78155	-17.40869	-17.40869	52.78	127.22	24.04	1.92443	0.47279
$(C-C (f))$	C ₁	-0.92918	-0.92918	-0.92918	-0.92918	-154.51399	0.91771	0.76763	-17.92866	-17.92866	50.04	129.96	22.66	1.94462	0.49298

Table 15.168. The energy parameters (eV) of functional groups of allyl sulfonides.

Parameters	C-S Group	SO Group	CH ₃ Group	CH ₂ Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
η_1	1	2	3	2	1	1	1	1	1	1	1
η_2	0	0	2	1	0	0	0	0	0	0	0
η_3	0	0	0	0	0	0	0	0	0	0	0
η_4	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
η_5	0.6951	1	1	1	1	1	1	1	1	1	1
η_6	1	1	1	1	1	1	1	1	1	1	1
η_7	1	1.20332	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_8	0	0	0	1	1	0	0	0	1	1	0
η_9	2	4	1	1	1	2	2	2	2	2	2
η_{10}	0	1	3	2	1	0	0	0	0	0	0
η_{11}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
η_{12}	0.6951	1	1	1	1	1	1	1	1	1	1
η_{13}	1	1	1	1	1	1	1	1	1	1	1
η_{14}	1	1.20332	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{15}	0	0	0	1	1	0	0	0	1	1	0
η_{16}	2	4	1	1	1	2	2	2	2	2	2
η_{17}	0	1	3	2	1	0	0	0	0	0	0
η_{18}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
η_{19}	0.6951	1	1	1	1	1	1	1	1	1	1
η_{20}	1	1	1	1	1	1	1	1	1	1	1
η_{21}	1	1.20332	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{22}	0	0	0	1	1	0	0	0	1	1	0
η_{23}	2	4	1	1	1	2	2	2	2	2	2
η_{24}	0	1	3	2	1	0	0	0	0	0	0
η_{25}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
η_{26}	0.6951	1	1	1	1	1	1	1	1	1	1
η_{27}	1	1	1	1	1	1	1	1	1	1	1
η_{28}	1	1.20332	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{29}	0	0	0	1	1	0	0	0	1	1	0
η_{30}	2	4	1	1	1	2	2	2	2	2	2
η_{31}	0	1	3	2	1	0	0	0	0	0	0
η_{32}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
η_{33}	0.6951	1	1	1	1	1	1	1	1	1	1
η_{34}	1	1	1	1	1	1	1	1	1	1	1
η_{35}	1	1.20332	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{36}	0	0	0	1	1	0	0	0	1	1	0
η_{37}	2	4	1	1	1	2	2	2	2	2	2
η_{38}	0	1	3	2	1	0	0	0	0	0	0
η_{39}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
η_{40}	0.6951	1	1	1	1	1	1	1	1	1	1
η_{41}	1	1	1	1	1	1	1	1	1	1	1
η_{42}	1	1.20332	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{43}	0	0	0	1	1	0	0	0	1	1	0
η_{44}	2	4	1	1	1	2	2	2	2	2	2
η_{45}	0	1	3	2	1	0	0	0	0	0	0
η_{46}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
η_{47}	0.6951	1	1	1	1	1	1	1	1	1	1
η_{48}	1	1	1	1	1	1	1	1	1	1	1
η_{49}	1	1.20332	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{50}	0	0	0	1	1	0	0	0	1	1	0
η_{51}	2	4	1	1	1	2	2	2	2	2	2
η_{52}	0	1	3	2	1	0	0	0	0	0	0
η_{53}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
η_{54}	0.6951	1	1	1	1	1	1	1	1	1	1
η_{55}	1	1	1	1	1	1	1	1	1	1	1
η_{56}	1	1.20332	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{57}	0	0	0	1	1	0	0	0	1	1	0
η_{58}	2	4	1	1	1	2	2	2	2	2	2
η_{59}	0	1	3	2	1	0	0	0	0	0	0
η_{60}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
η_{61}	0.6951	1	1	1	1	1	1	1	1	1	1
η_{62}	1	1	1	1	1	1	1	1	1	1	1
η_{63}	1	1.20332	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{64}	0	0	0	1	1	0	0	0	1	1	0
η_{65}	2	4	1	1	1	2	2	2	2	2	2
η_{66}	0	1	3	2	1	0	0	0	0	0	0
η_{67}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
η_{68}	0.6951	1	1	1	1	1	1	1	1	1	1
η_{69}	1	1	1	1	1	1	1	1	1	1	1
η_{70}	1	1.20332	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{71}	0	0	0	1	1	0	0	0	1	1	0
η_{72}	2	4	1	1	1	2	2	2	2	2	2
η_{73}	0	1	3	2	1	0	0	0	0	0	0
η_{74}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
η_{75}	0.6951	1	1	1	1	1	1	1	1	1	1
η_{76}	1	1	1	1	1	1	1	1	1	1	1
η_{77}	1	1.20332	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{78}	0	0	0	1	1	0	0	0	1	1	0
η_{79}	2	4	1	1	1	2	2	2	2	2	2
η_{80}	0	1	3	2	1	0	0	0	0	0	0
η_{81}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
η_{82}	0.6951	1	1	1	1	1	1	1	1	1	1
η_{83}	1	1	1	1	1	1	1	1	1	1	1
η_{84}	1	1.20332	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{85}	0	0	0	1	1	0	0	0	1	1	0
η_{86}	2	4	1	1	1	2	2	2	2	2	2
η_{87}	0	1	3	2	1	0	0	0	0	0	0
η_{88}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
η_{89}	0.6951	1	1	1	1	1	1	1	1	1	1
η_{90}	1	1	1	1	1	1	1	1	1	1	1
η_{91}	1	1.20332	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{92}	0	0	0	1	1	0	0	0	1	1	0
η_{93}	2	4	1	1	1	2	2	2	2	2	2
η_{94}	0	1	3	2	1	0	0	0	0	0	0
η_{95}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
η_{96}	0.6951	1	1	1	1	1	1	1	1	1	1
η_{97}	1	1	1	1	1	1	1	1	1	1	1
η_{98}	1	1.20332	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
η_{99}	0	0	0	1	1	0	0	0	1	1	0
η_{100}	2	4	1	1	1	2	2	2	2	2	2

Table 15.169. The total bond energies of allyl sulfonides calculated using the functional group composition and the energies of Table 15.168 compared to the experimental values [3].

Formula	C-S Group	SO Group	CH ₃ Group	CH ₂ Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₃ H ₇ SO	2	1	2	0	0	0	0	0	0	0	0	33.32400	33.435	-0.00233
C ₃ H ₇ SO	2	1	2	2	0	2	0	0	0	0	0	39.83900	39.891	0.00045
C ₃ H ₇ SO	2	1	2	4	0	0	0	0	0	0	0	84.13350	84.294	0.00163

Table 15.170. The bond angle parameters of allyl sulfoxides and experimental values [1]. In the calculation of θ_i , the parameters from the preceding angle were used. E_f is $E_f(\text{atom} - \text{atom}, \text{exp}, \text{AO})$.

Atom angle	$2\alpha_1$ Bond ($^\circ$)	$2\alpha_2$ Bond ($^\circ$)	$2\alpha_3$ Bond ($^\circ$)	$E_{\text{calc}}^{\text{atom}}$ Atom 1 (eV)	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{\text{calc}}^{\text{atom}}$ Atom 2 (eV)	Atom 2 Hybridization Designation (Table 15.3.A)	C_1	C_2	C_3	ζ_1	ζ_2	E_f (eV)	θ_1 ($^\circ$)	θ_2 ($^\circ$)	Cal. θ ($^\circ$)	Exp. θ ($^\circ$)
$\angle C_1 S C_2$	3.34541	3.34541	4.9800	-16.47951	21	-16.47951	21	0.82562	1	1	1	0.82562	-1.83536			96.20	96.6 (dimethyl sulfoxide)
$\angle C_1 S O$	3.34541	2.81792	4.9808	-15.18506	2	-15.18506	O	0.83393	1	1	1	0.83393	-1.63376			106.88	106.7 (dimethyl sulfoxide)
$\angle H C_1 H$	2.11106	2.11106	3.4252	-15.73493	7	H	H	0.80359	1	1	0.75	1.13796	0			108.44	107 (propane)
$\angle C_1 C_2 C_3$																	113 (propane)
$\angle C_1 C_2 H$																	113.8 (propane)
$\angle H C_2 H$	2.09711	2.09711	3.4252	-15.73493	7	H	H	0.80359	1	1	0.75	1.13796	0	69.51		110.49	113.8 (propane)
$\angle C_1 C_3 C_2$																	111.4 (propane)
$\angle C_1 C_3 H$																	111.4 (propane)
$\angle H C_3 H$	2.09547	2.09547	4.7958	-16.66412	15	C_3	75	0.81549	1	1	1	0.81549	-1.83536	70.56		109.50	110.3 (dimethyl sulfoxide)
$\angle C_1 C_2 H$	2.09547	2.11223	4.1633	-15.59033	5	C_2	1	0.87495	1	0.75	1	1.04887	0	70.56		109.44	
$\angle C_1 C_3 H$	2.09547	2.09711	4.1633	-15.59033	5	C_3	1	0.87495	1	0.75	1	1.04887	0	70.56		109.44	
$\angle C_2 C_3 C_1$	2.09547	2.09711	4.1633	-15.59033	5	C_3	1	0.87495	1	0.75	1	1.04887	0			110.67	110.3 (propane)
$\angle C_2 C_3 H$	2.09547	2.09711	4.1633	-15.59033	5	C_3	1	0.87495	1	0.75	1	1.04887	0			110.76	
$\angle C_3 C_2 C_1$	2.09327	2.09327	4.7958	-15.59033	5	C_2	1	0.87495	1	0.75	1	1.04887	-1.83536			111.27	111.4 (propane)
$\angle C_3 C_2 H$																111.27	111.4 (propane)
$\angle C_3 C_1 C_2$														72.50		107.50	

DIMETHYL SULFOXIDE DIHEDRAL ANGLE

The dihedral angle $\theta_{\angle S=O/CSC'}$ between the plane defined by the CSC MO comprising a linear combination of two $S-C$ -bond MOs and a line defined by the $S=O$ -bond MO where S is the central atom is calculated using the results given in Table 15.170 and Eqs. (15.105-15.108). The distance d_1 along the bisector of $\theta_{\angle CSC'}$ from S to the internuclear-distance line between C and $C', 2c'_{C-C}$, is given by

$$d_1 = 2c'_{S-C} \cos \frac{\theta_{\angle CSC'}}{2} = 4.9800a_0 \cos \frac{96.20^\circ}{2} = 2.23423a_0 \quad (15.134)$$

where $2c'_{S-C}$ is the internuclear distance between S and C . The atoms C, C' , and O define the base of a pyramid. Then, the pyramidal angle $\theta_{\angle COC'}$ can be solved from the internuclear distances between C and $C', 2c'_{C-C}$, and between C and $O, 2c'_{C-O}$, using the law of cosines (Eq. (15.106)):

$$\begin{aligned} \theta_{\angle COC'} &= \cos^{-1} \left(\frac{(2c'_{C-O})^2 + (2c'_{C-O})^2 - (2c'_{C-C})^2}{2(2c'_{C-O})(2c'_{C-O})} \right) \\ &= \cos^{-1} \left(\frac{(4.95984)^2 + (4.95984)^2 - (4.9800)^2}{2(4.95984)(4.95984)} \right) \\ &= 60.27^\circ \end{aligned} \quad (15.135)$$

Then, the distance d_2 along the bisector of $\theta_{\angle COC'}$ from O to the internuclear-distance line $2c'_{C-C}$, is given by

$$d_2 = 2c'_{C-O} \cos \frac{\theta_{\angle COC'}}{2} = 4.95984a_0 \cos \frac{60.27^\circ}{2} = 4.28952a_0 \quad (15.136)$$

The lengths d_1, d_2 , and $2c'_{S=O}$ define a triangle wherein the angle between d_1 and the internuclear distance between O and $S, 2c'_{S=O}$, is the dihedral angle $\theta_{\angle S=O/CSC'}$ that can be solved using the law of cosines (Eq. (15.108)):

$$\begin{aligned} \theta_{\angle S=O/CSC'} &= \cos^{-1} \left(\frac{d_1^2 + (2c'_{S=O})^2 - d_2^2}{2d_1(2c'_{S=O})} \right) \\ &= \cos^{-1} \left(\frac{(2.23423)^2 + (2.81792)^2 - (4.28952)^2}{2(2.23423)(2.81792)} \right) \\ &= 115.74^\circ \end{aligned} \quad (15.137)$$

The experimental [1] dihedral angle $\theta_{\angle S=O/CSC}$ is

$$\theta_{\angle S=O/CSC} = 115.5^\circ$$

(15.138)

SULFITES ($C_nH_{2n+2}(SO_3)_m$, $n=2,3,4,5\ldots\infty$)

The alkyl sulfites, $C_nH_{2n+2}(SO_3)_m$, comprise a $C-O-SO-O-C$ moiety that comprises two types $C-O$ functional groups, one for methyl and one for alkyl, and $O-S$ and SO functional groups. The alkyl portion of the alkyl sulfite may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfites are equivalent to those in branched-chain alkanes.

The SO functional group is equivalent to that of sulfoxides with $E_r(atom-atom,msp^3.AO)=0$ as given in the Sulfoxides section. The methyl and alkyl $C-O$ functional groups having $E_r(atom-atom,msp^3.AO)=-1.44915\text{ eV}$ and $E_r(atom-atom,msp^3.AO)=-1.65376\text{ eV}$, respectively, are equivalent to the corresponding ether groups given in the Ethers section except for the energy terms corresponding to oscillation of the bond in the transition state.

The electron configuration of oxygen is $1s^22s^22p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state 3P_2 . The SO functional group comprises a double bond between the S atom and the two unpaired electrons of O . The S atom also forms single bonds with two additional oxygen atoms that are each further bound to methyl or alkyl groups. The first bond-order bonding in the $O-S$ groups is between the sulfur atom and a $O2p$ AO of each oxygen of the two bonds. The formation of these four bonds with the sulfur atom is permitted by the hybridization of the four electrons of the $S3p$ shell to give the orbital arrangement given by Eq. (15.129). Then, the Coulombic energy $E_{Coulomb}(S,3sp^3)$ of the outer electron of the $S3sp^3$ shell given by Eq. (15.120) with $r_{3sp^3}=1.17585a_0$ (Eq. (15.119)) is -11.57099 eV . Using Eq. (15.16) with the radius of the

sulfur atom $r_{16} = 1.32010a_0$ given by Eq. (10.341), the energy $E(S3sp^3)$ of the outer electron of the $S3sp^3$ shell given by the sum of $E_{Coulomb}(S3sp^3)$ and $E(magnetic)$ is $E(S3sp^3) = -11.52126 \text{ eV}$ (Eq. (15.130)).

Thus, the $O-S$ group is solved as an energy minimum by hybridizing the four $S3p$ 5 electrons to form a $S3sp^3$ shell, and the sharing of electrons between the $O2p$ AO and the $S3sp^3$ HO to form a MO permits each participating orbital to decrease in radius and energy. As in the case of thiols, sulfides, disulfides, and sulfoxides, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_1 and c_2 are equal to one in Eq. (15.52), and the energy matching condition is determined by the C_2 10 parameter. Each $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \text{ eV}$ (Eq. (15.25)), and the S HO has an energy of $E(S3sp^3) = -11.52126 \text{ eV}$. To meet the equipotential condition of the union of the $O-S$ H_2 -type-ellipsoidal-MO with these orbitals with the oxygen that further bonds to a $C2sp^3$ HO, the hybridization factor C_2 of Eq. (15.52) for the $O-S$ -bond MO given by Eqs. 15 (15.68) and (15.70) is

$$\begin{aligned} C_2(S3sp^3 \text{ to } O \text{ to } C2sp^3 HO) &= \frac{E(S,3sp^3)}{E(O,2p)} c_2(C2sp^3 HO) \\ &= \frac{-11.52126 \text{ eV}}{-13.61806 \text{ eV}} (0.91771) \\ &= 0.77641 \end{aligned} \quad (15.139)$$

As in the case of thiols, sulfides, disulfides, and sulfoxides, with the energy of S matched to the Coulombic energy between the electron and proton of H , the energy of the $O-S$ -bond MO is the sum of the component energies of the H_2 -type ellipsoidal MO given in 20 Eq. (15.42) with $E(AO/HO) = 0$ and $E_T(AO/HO) = \Delta E_{H_2MO}(AO/HO)$. For sulfites, $\Delta E_{H_2MO}(AO/HO) = -0.92918 \text{ eV}$ and equivalently, $E_T(atom - atom, msp^3, AO) = -0.92918 \text{ eV}$ (Eq. (14.513)) due to the maximum energy match with the oxygen AO as in the case with carboxylic acid esters.

The symbols of the functional groups of branched-chain alkyl sulfites are given in Table 15.177. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfites are given in Tables 15.178, 15.179, and 15.180, respectively. The total energy of each alkyl sulfite given in Table 5 15.175 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.180 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfites determined using Eqs. (15.79-15.108) are given in Table 15.182.

Table 15.177. The symbols of functional groups of alkyl sulfites.

Functional Group	Group Symbol
C-O (methyl)	$C-O$ (i)
C-O (alkyl)	$C-O$ (ii)
O-SO ₂	$O-S$
SO	SO
CH ₃ group	$C-H$ (CH ₃)
CH ₂ group	$C-H$ (CH ₂)
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.178. The geometrical bond parameters of alkyl sulfides and experimental values [1].

Parameter	C-O (I) Group	C-O (II) Group	O-S	SO	C-H (CH ₃) Group	C-H (CH ₂) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
σ (Å)	1.80717	1.79473	1.70259	1.98317	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
c' (Å)	1.34431	1.33968	1.48102	1.40896	1.04856	1.05555	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	1.42276	1.41785	1.56744	1.49118	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $2c'$ (Å)			1.574 (H ₂ SO ₄)	1.485 (dimethyl sulfoxide)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutene)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
h, c' (Å)	1.20776	1.19429	0.84059	1.39847	1.27295	1.29569	1.29974	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
ϵ	0.74388	0.74643	0.86966	0.70974	0.65380	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.179. The MO to HO intercept geometrical bond parameters of allyl sulfates. E_p is $E_p(\text{atom} - \text{atom}, \text{resp. AO})$.

Bond	Atom	E_p (eV) Bond 1	E_p (eV) Bond 2	E_p (eV) Bond 3	E_p (eV) Bond 4	Final Total Energy C2sp ² (eV)	r_{bond} (a ₀)	E_{bond} (eV) Final	$E(\text{C2sp}^2)$ (eV) Final	θ_i (°)	θ_j (°)	d_i (a ₀)	d_j (a ₀)
(RO) ₂ S=O ₂	S	0	-0.46439	-0.46439	0		0.6339	-15.75403		74.56	101.44	1.58026	0.17130
(RO) ₂ S=O ₂	O ₂	0	0	0	0		0.91771	-16.82575		84.06	93.94	1.50400	0.09304
CH ₃ O ₂ -S(O)OR	N	-0.46439	-0.46439	0	0		0.6339	-15.75403		126.64	53.22	0.96531	0.51381
CH ₃ O ₂ -S(O)OR	O ₂	-0.46439	-0.72457	0	0		0.84937	-16.01402		126.03	53.97	0.98133	0.49969
(C-C-O (b))	O ₂	-0.46439	-0.72457	0	0		0.84937	-16.01402		125.77	54.23	0.98133	0.49969
CH ₃ O ₂ -S(O)OR	O ₂	-0.46439	-0.72457	0	0		0.84937	-16.01402		93.85	86.15	1.38771	0.05700
H ₂ C ₂ -O ₂ S(O)OR	O ₂	-0.72457	-0.46439	0	0		0.84937	-16.01402		93.85	86.15	1.38771	0.05700
(C-C-O (b))	O ₂	-0.72457	-0.46439	0	0		0.84937	-16.01402		93.85	86.15	1.38771	0.05700
H ₂ C ₂ -O ₂ S(O)OR	C ₂	-0.72457	0	0	0	-153.4025	0.91771	-15.53033	-15.33946	84.02	46.10	1.23319	0.09112
(C-C-O (b))	O ₂	-0.72457	0	0	0		0.84937	-16.01402		94.50	84.50	1.27143	0.06624
CH ₃ C ₂ -O ₂ S(O)OR	O ₂	-0.72457	-0.46439	0	0		0.84937	-16.01402		92.41	87.59	1.38512	0.03456
CH ₃ C ₂ -O ₂ S(O)OR	C ₂	-0.72457	-0.72457	0	0	-153.37175	0.91771	-16.53811	-16.39093	87.59	43.35	1.38512	0.03456
(C-C-O (b))	O ₂	-0.72457	-0.72457	0	0		0.84937	-16.01402		77.49	102.51	1.23564	0.18708
C-H (CH ₂)	C	-0.92918	0	0	0	-152.54487	0.91771	-15.75493	-15.56407	98.47	111.53	1.35466	0.29923
C-H (CH ₂)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.49725	-16.49725	61.10	118.90	1.42988	0.37226
C-H (CH ₂)	C	-0.92918	-0.92918	0	0	-154.40324	0.91771	-17.61330	-17.42344	116.18	30.08	1.38379	0.38106
H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	0	0	0	-153.54417	0.91771	-15.75493	-15.56407	98.47	111.53	1.35466	0.29923
H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.49725	-16.49725	61.10	118.90	1.42988	0.37226
H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-154.40324	0.91771	-17.61330	-17.42344	116.18	30.08	1.38379	0.38106
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.54417	0.91771	-15.75493	-15.56407	98.47	111.53	1.35466	0.29923
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.49725	-16.49725	61.10	118.90	1.42988	0.37226
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-154.40324	0.91771	-17.61330	-17.42344	116.18	30.08	1.38379	0.38106
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.54417	0.91771	-15.75493	-15.56407	98.47	111.53	1.35466	0.29923
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.49725	-16.49725	61.10	118.90	1.42988	0.37226
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-154.40324	0.91771	-17.61330	-17.42344	116.18	30.08	1.38379	0.38106
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.54417	0.91771	-15.75493	-15.56407	98.47	111.53	1.35466	0.29923
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.49725	-16.49725	61.10	118.90	1.42988	0.37226
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-154.40324	0.91771	-17.61330	-17.42344	116.18	30.08	1.38379	0.38106
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.54417	0.91771	-15.75493	-15.56407	98.47	111.53	1.35466	0.29923
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.49725	-16.49725	61.10	118.90	1.42988	0.37226
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-154.40324	0.91771	-17.61330	-17.42344	116.18	30.08	1.38379	0.38106
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.54417	0.91771	-15.75493	-15.56407	98.47	111.53	1.35466	0.29923
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.49725	-16.49725	61.10	118.90	1.42988	0.37226
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-154.40324	0.91771	-17.61330	-17.42344	116.18	30.08	1.38379	0.38106
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.54417	0.91771	-15.75493	-15.56407	98.47	111.53	1.35466	0.29923
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.49725	-16.49725	61.10	118.90	1.42988	0.37226
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-154.40324	0.91771	-17.61330	-17.42344	116.18	30.08	1.38379	0.38106
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.54417	0.91771	-15.75493	-15.56407	98.47	111.53	1.35466	0.29923
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.49725	-16.49725	61.10	118.90	1.42988	0.37226
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-154.40324	0.91771	-17.61330	-17.42344	116.18	30.08	1.38379	0.38106
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.54417	0.91771	-15.75493	-15.56407	98.47	111.53	1.35466	0.29923
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.49725	-16.49725	61.10	118.90	1.42988	0.37226
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-154.40324	0.91771	-17.61330	-17.42344	116.18	30.08	1.38379	0.38106
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.54417	0.91771	-15.75493	-15.56407	98.47	111.53	1.35466	0.29923
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.49725	-16.49725	61.10	118.90	1.42988	0.37226
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-154.40324	0.91771	-17.61330	-17.42344	116.18	30.08	1.38379	0.38106
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.54417	0.91771	-15.75493	-15.56407	98.47	111.53	1.35466	0.29923
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.49725	-16.49725	61.10	118.90	1.42988	0.37226
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-154.40324	0.91771	-17.61330	-17.42344	116.18	30.08	1.38379	0.38106
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.54417	0.91771	-15.75493	-15.56407	98.47	111.53	1.35466	0.29923
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.49725	-16.49725	61.10	118.90	1.42988	0.37226
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-154.40324	0.91771	-17.61330	-17.42344	116.18	30.08	1.38379	0.38106
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.54417	0.91771	-15.75493	-15.56407	98.47	111.53	1.35466	0.29923
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.49725	-16.49725	61.10	118.90	1.42988	0.37226
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-154.40324	0.91771	-17.61330	-17.42344	116.18	30.08	1.38379	0.38106
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.54417	0.91771	-15.75493	-15.56407	98.47	111.53	1.35466	0.29923
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.49725	-16.49725	61.10	118.90	1.42988	0.37226
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-154.40324	0.91771	-17.61330	-17.42344	116.18	30.08	1.38379	0.38106
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.54417	0.91771	-15.75493	-15.56407	98.47	111.53	1.35466	0.29923
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.49725	-16.49725	61.10	118.90	1.42988	0.37226
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-154.40324	0.91771	-17.61330	-17.42344	116.18	30.08	1.38379	0.38106
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.54417	0.91771	-15.75493	-15.56407	98.47	111.53	1.35466	0.29923
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.49725	-16.49725	61.10	118.90	1.42988	0.37226
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-154.40324	0.91771	-17.61330	-17.42344	116.18	30.08	1.38379	0.38106
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.54417	0.91771	-15.75493	-15.56407	98.47	111.53	1.35466	0.29923
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.49725	-16.49725	61.10	118.90	1.42988	0.37226
R-H ₂ C ₂ H ₂ H ₂ -	C ₂	-0.92918	-0.92918	0	0	-154.40324	0.91771	-17.61330	-17.42344	116.18	30.08	1.38379	0.38106
R-H ₂ C ₂ H ₂ H ₂ -	C<												

Table 15.180. The energy parameters (eV) of functional groups of alkyl sulfites.

Parameters	C-O (i)	C-O (ii)	O-S	SO	CH ₃	CH ₂	C-H	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)
η_1	1	1	1	2	3	2	1	1	1	1	1	1	1
η_2	0	0	0	0	2	1	0	0	0	0	0	0	0
η_3	0	0	0	0	0	0	0	0	0	0	0	0	0
ζ_1	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
ζ_2	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_3	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_4	0.85395	0.85395	1	1.20532	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
ζ_5	0	0	0	0	0	1	1	0	0	0	1	1	0
ζ_6	2	2	2	4	1	1	1	2	2	2	2	2	2
ζ_7	0	0	0	1	3	2	1	0	0	0	0	0	0
ζ_8	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
ζ_9	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{10}	-33.15757	-33.47304	-48.93512	-82.63003	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214
ζ_{11}	10.12103	10.15605	9.18680	19.11323	38.92728	25.78002	12.87680	9.33352	9.33352	9.33352	9.33352	9.33352	9.33352
ζ_{12}	9.17389	9.32337	14.36741	20.81183	32.53918	21.06675	10.48382	6.77464	6.77464	6.77464	6.77464	6.77464	6.77464
ζ_{13}	-4.58695	-4.66268	-7.18371	-10.40392	-16.56957	-10.53337	-5.24291	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732
ζ_{14}	-14.63489	-14.63489	0	-11.57126	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
ζ_{15}	-1.44915	-1.65376	-0.92918	-1.16125	0	0	0	0	0	0	0	0	0
ζ_{16}	-13.18374	-12.98113	0.92518	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
ζ_{17}	-31.63333	-31.63344	-31.63543	-63.27088	-67.69451	-49.66493	-31.63353	-31.63357	-31.63357	-31.63357	-31.63357	-31.63357	-31.63357
ζ_{18}	-1.44915	-1.65376	-0.92918	0	0	0	0	-1.85856	-1.85856	-1.85856	-1.85856	-1.85856	-1.85856
ζ_{19}	-33.08452	-33.28912	-32.56435	-63.27074	-67.69450	-49.66493	-31.63357	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373
ζ_{20}	22.0240	12.1583	14.96660	21.99527	24.9286	24.2751	24.1759	9.43699	9.43699	9.43699	9.43699	9.43699	9.43699
ζ_{21}	-0.24921	-0.18631	-0.30214	-0.21348	-0.23532	-0.25017	-0.24966	-0.16515	-0.16515	-0.16515	-0.16515	-0.16515	-0.16515
ζ_{22}	0.13663	0.13663	0.08679	0.12832	0.35532	0.35532	0.35532	0.12312	0.12312	0.12312	0.12312	0.12312	0.12312
ζ_{23}	-0.18089	-0.11799	-0.23875	-0.14932	-0.22757	-0.14502	-0.07200	-0.10359	-0.10359	-0.10359	-0.10359	-0.10359	-0.10359
ζ_{24}	0.14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
ζ_{25}	-33.26541	-33.40711	-32.82330	-63.56937	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732
ζ_{26}	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
ζ_{27}	0	0	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
ζ_{28}	3.99563	4.13733	3.55332	3.86856	12.49186	7.82016	3.22601	4.32754	4.29211	3.97398	4.17931	3.62128	3.91734

Table 15.181. The total bond energies of alkyl sulfites calculated using the functional group composition and the energies of Table 15.180 compared to the experimental values [3].

Formula	C-O (i)	C-O (ii)	O-S	SO	CH ₃	CH ₂	C-H	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH ₃ SO ₃	2	0	2	1	2	0	0	0	0	0	0	0	0	65.4019	65.4019	0.0000
CH ₃ SO ₂	0	2	2	1	2	0	0	0	0	0	0	0	0	68.44	68.44	0.00143
CH ₃ SO	0	2	2	1	2	0	0	0	0	0	0	0	0	117.1819	117.181	0.0009

SULFATES ($C_nH_{2n+2}(SO_4)_m$, $n = 2, 3, 4, 5, \dots, \infty$)

The alkyl sulfates, $C_nH_{2n+2}(SO_4)_m$, comprise a $C-O-SO_2-O-C$ moiety that comprises two types $C-O$ functional groups, one for methyl and one for alkyl, and $O-S$ and SO_2 functional groups. The alkyl portion of the alkyl sulfate may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfates are equivalent to those in branched-chain alkanes.

The methyl and alkyl $C-O$ functional groups having $E_r(atom-atom, msp^3.AO) = -1.44915 \text{ eV}$ and $E_r(atom-atom, msp^3.AO) = -1.65376 \text{ eV}$, respectively, are equivalent to the corresponding groups given in the Sulfites section. The $O-S$ functional group having $E_r(atom-atom, msp^3.AO) = -0.92918 \text{ eV}$ is equivalent to that given in the Sulfites section. The SO_2 functional group is equivalent to that of sulfones with $E_r(atom-atom, msp^3.AO) = 0$ as given in the Sulfones section.

The symbols of the functional groups of branched-chain alkyl sulfates are given in Table 15.183. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfates are given in Tables 15.184, 15.185, and 15.186, respectively. The total energy of each alkyl sulfate given in Table 15.187 was calculated as the sum over the integer multiple of each $E_D(group)$ of Table 15.186 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfates determined using Eqs. (15.79-15.108) are given in Table 15.188.

Table 15.185. The MO to HO intercept geometrical bond parameters of alkyl sulfates. E_p is $E_p(\text{atom} - \text{atom}, \text{map}, \text{AO})$.

Bond	Atom	E_p (eV) Bond 1	E_p (eV) Bond 2	E_p (eV) Bond 3	E_p (eV) Bond 4	Final Total Energy E_{Total} (eV)	r_{map} (a_0)	r_{map} (a_0)	E_{Total} (eV) Final	θ^* ($^\circ$)	θ_s ($^\circ$)	θ_d ($^\circ$)	d_s (a_0)
$(RO)_2(O)_2S=O_2$	S	0	0	-0.46459	-0.46459	-15.74693	1.32010	0.80359	-15.74693	90.46	89.34	43.13	1.35635
$(RO)_2(O)_2S=O_2$	O	0	0	0	0	-15.83575	1.00000	0.91771	-15.83575	95.05	84.93	46.36	1.28246
$CH_3O-S(O)_2OR^*$	S	-0.46459	-0.46459	0	0	-15.74693	1.32010	0.80359	-15.74693	126.68	53.32	55.47	0.96321
$CH_3O-S(O)_2OR^*$	O	-0.46459	-0.72457	0	0	-16.01492	1.00000	0.84957	-16.01492	126.03	53.97	54.81	0.98133
$(C-O)(II)$	O	-0.46459	-0.82688	0	0	-16.11722	1.00000	0.84418	-16.11722	125.77	54.23	54.56	0.98753
$H_2C-O-S(O)_2OR^*$	O	-0.72457	-0.46459	0	0	-16.01492	1.00000	0.84957	-16.01492	93.85	86.15	44.37	1.28731
$H_2C-O-S(O)_2OR^*$	C	-0.72457	0	0	0	-15.53033	0.91771	0.87495	-15.53033	95.98	84.02	46.10	1.25319
$RH_2C-O-S(O)_2OR^*$	O	-0.82688	-0.46459	0	0	-16.11722	1.00000	0.84418	-16.11722	94.30	83.50	44.80	1.27943
$RH_2C-O-S(O)_2OR^*$	C	-0.82688	-0.92918	0	0	-16.58181	0.91771	0.82053	-16.58181	92.41	87.59	43.35	1.30512
$(C-H)(CH_3)$	C	-0.92918	0	0	0	-15.54487	0.91771	0.86359	-15.54487	77.49	102.51	41.48	1.23164
$C-H(CH_3)$	C	-0.92918	-0.92918	0	0	-15.47406	0.91771	0.81549	-15.47406	68.47	111.53	35.84	1.35486
$C-H(CH_3)$	C	-0.92918	-0.92918	-0.92918	0	-15.440324	0.91771	0.77247	-15.440324	61.10	118.90	31.37	1.42948
$H_2C-C_2H_4CH_2-$	C	-0.92918	0	0	0	-15.54487	0.91771	0.86359	-15.54487	62.82	116.18	30.03	1.83879
$(C-C)(II)$	C	-0.92918	-0.92918	0	0	-16.68412	0.91771	0.81549	-16.68412	56.41	123.59	26.06	1.90890
$R-H_2C-C_2H_4CH_2-$	C	-0.92918	-0.92918	0	0	-17.61330	0.91771	0.77247	-17.61330	48.30	131.70	21.90	1.97162
$R-H_2C-C_2H_4CH_2-$	C	-0.92918	-0.72457	-0.72457	-0.72457	-17.92866	0.91771	0.75889	-17.92866	48.31	131.79	21.74	1.95754
$isoC_2H_5-C_2H_4CH_2-$	C	-0.92918	-0.92918	-0.92918	0	-17.61330	0.91771	0.77247	-17.61330	48.30	131.70	21.90	1.97162
$isoC_2H_5-C_2H_4CH_2-$	C	-0.72457	-0.72457	-0.72457	-0.72457	-17.60869	0.91771	0.75889	-17.60869	50.04	129.96	22.66	1.94462
$isoC_2H_5-C_2H_4CH_2-$	C	-0.72457	-0.92918	-0.92918	0	-17.21783	0.91771	0.78155	-17.21783	52.78	127.22	24.04	1.92443
$(C-C)(II)$	C	-0.72457	-0.72457	-0.72457	-0.72457	-17.92866	0.91771	0.75889	-17.92866	50.04	129.96	22.66	1.94462

Table 15.186. The energy parameters (eV) of functional groups of alkyl sulfates.

Parameters	C-O (i)	C-O (ii)	O-S	SO ₂	CH ₃	CH ₂	C-H	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)
Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
μ_1	1	1	1	4	3	2	1	1	1	1	1	1	1
μ_2	0	0	0	0	2	1	0	0	0	0	0	0	0
μ_3	0	0	0	0	0	0	0	0	0	0	0	0	0
μ_4	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
μ_5	1	1	0.7641	1	1	1	1	1	1	1	1	1	1
μ_6	1	1	1	1	1	1	1	1	1	1	1	1	1
μ_7	0.85395	0.85395	1	1.20632	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
μ_8	0	0	0	1	0	1	1	0	0	0	1	1	0
μ_9	2	2	2	8	1	1	1	2	2	2	2	2	2
μ_{10}	0	0	0	1	3	2	1	0	0	0	0	0	0
μ_{11}	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
μ_{12}	1	1	0.7641	1	1	1	1	1	1	1	1	1	1
μ_{13}	1	1	1	1	1	1	1	1	1	1	1	1	1
μ_{14}	33.15757	33.47304	48.93512	-180.36454	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
μ_{15}	10.12103	10.15605	9.18680	39.92103	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
μ_{16}	9.17389	9.52537	14.36741	48.52397	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
μ_{17}	-4.38695	-4.66268	-7.18371	-24.26198	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
μ_{18}	-14.63489	-14.63489	0	-11.52126	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
μ_{19}	-1.44915	-1.65376	-0.92918	-1.16125	-15.56407	0	0	0	0	0	0	0	0
μ_{20}	-13.18574	-12.98113	0.92918	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
μ_{21}	-31.63533	-31.63544	-31.63543	-126.54154	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
μ_{22}	-1.44915	-1.65376	-0.92918	0	0	0	0	-1.83836	-1.83836	-1.44915	-1.83836	-1.44915	-1.44915
μ_{23}	-33.08452	-33.28912	-32.56455	-126.54147	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
μ_{24}	22.0240	12.1583	33.4164	11.5378	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
μ_{25}	14.49660	8.00277	21.99527	7.59437	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
μ_{26}	-0.24921	-0.18631	-0.30214	-0.17247	-0.23332	-0.23017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
μ_{27}	0.13663	0.13663	0.08679	0.12832	0.35532	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.12312	0.12312
μ_{28}	[21]	[21]	[42]	[43]	(Eq. (13.458))	(Eq. (13.458))	(Eq. (13.458))	[21]	[41]	[51]	[21]	[21]	[21]
μ_{29}	-0.18089	-0.11799	-0.25875	-0.10831	-0.27377	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
μ_{30}	0.14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
μ_{31}	-33.26541	-33.40711	-32.82330	-126.57472	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.26541	-33.59732	-33.26541	-33.26541
μ_{32}	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
μ_{33}	0	0	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
μ_{34}	3.99563	4.13733	3.55352	8.61994	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.187. The total bond energies of alkyl sulfates calculated using the functional group composition and the energies of Table 15.186 compared to the experimental values [3].

Formula	Name	C-O (i)	C-O (ii)	O-S	SO ₂	CH ₃	CH ₂	C-H	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH ₃ SO ₃	Dimethyl sulfate	2	0	2	1	2	0	0	0	0	0	0	0	0	48.714	48.714	0.00018
CH ₃ SO ₂	Dimethyl sulfate	0	2	2	1	2	0	2	0	0	0	0	0	0	73.3077	73.346	0.00061
CH ₃ SO ₃	Dimethyl sulfate	0	0	2	1	2	0	4	0	0	0	0	0	0	97.6167	97.609	-0.00008

NITROALKANES ($C_n H_{2n+2-m} (NO_2)_m$, $n = 1, 2, 3, 4, 5, \dots, \infty$)

The nitroalkanes, $C_n H_{2n+2-m} (NO_2)_m$, comprise a NO_2 functional group and a $C-N$ functional group. The alkyl portion of the nitroalkane may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n -alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2 CH$) and t-butyl ($(CH_3)_3 C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in nitroalkanes are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^2 2s^2 2p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state 3P_2 . The electron configuration of nitrogen is $1s^2 2s^2 2p^3$, and the orbital arrangement given by Eq. (10.134) has three unpaired electrons corresponding to the ground state $^4S_{3/2}$. The bonding in the nitro (NO_2) functional group is similar to that in the SO_2 group given previously. It also has similarities to the bonding in the carbonyl functional group. In the NO_2 group, the two unpaired electrons of the O atoms form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a linear combination of two bonds, each of bond order two involving the nitrogen AOs and oxygen AOs of both oxygen atoms. The nitrogen atom is then energy matched to the $C2sp^3$ HO. In nitroalkanes, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C, 2sp^3) = -14.63489 \text{ eV}$ (Eq. (15.25)), the N AO has an energy of $E(N) = -14.53414 \text{ eV}$, and the O AO has an energy of $E(O) = -13.61806 \text{ eV}$ [38]. To meet the equipotential condition of the union of the $N=O$ H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $N=O$ -bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(O \text{ to } N2p \text{ to } C2sp^3 HO) &= \frac{E(O)}{E(N)} c_2(C2sp^3 HO) \\ &= \frac{-13.61806 \text{ eV}}{-14.53414 \text{ eV}} (0.91771) \\ &= 0.85987 \end{aligned} \quad (15.140)$$

Since there are two O atoms in a linear combination that comprises the bonding of the NO_2 group, the unpaired electrons of each O cancel each others effect such that E_{mag} is not subtracted from the total energy of NO_2 . Additionally, $E_T(atom - atom, msp^3, AO) = -3.71673 \text{ eV} = 4(-0.92918 \text{ eV})$ (Eq. (14.513)) is the maximum
 5 given the bonding involves four electrons comprising two bonds, each having a bond order of one.

The $C-N$ group is equivalent to that of primary amines except that the energies corresponding to vibration in the transition state are matched to a nitroalkane and $\Delta E_{H_2MO}(AO/HO) = -0.72457 \text{ eV}$ for nitroalkane and $\Delta E_{H_2MO}(AO/HO) = -1.44915 \text{ eV}$ for
 10 primary amines. Whereas, $E_T(atom - atom, msp^3, AO) = -1.44915 \text{ eV}$ for both functional groups. This condition matches the energy of the $C-N$ group with the NO_2 having $\Delta E_{H_2MO}(AO/HO) = 0$.

The symbols of the functional groups of branched-chain nitroalkanes are given in Table 15.189. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and
 15 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of nitroalkanes are given in Tables 15.190, 15.191, and 15.192, respectively. The total energy of each nitroalkane given in Table 15.193 was calculated as the sum over the integer multiple of each $E_{D(Group)}$ of Table 15.192 corresponding to functional-group composition of the molecule. E_{mag} given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of nitroalkanes determined using
 20 Eqs. (15.79-15.108) are given in Table 15.194.

Table 15.189. The symbols of functional groups of nitroalkanes.

Functional Group	Group Symbol
NO_2 group	NO_2
$C-N$	$C-N$
CH_3 group	$C-H(CH_3)$
CH_2 group	$C-H(CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C(a)$
CC bond (iso-C)	$C-C(b)$
CC bond (tert-C)	$C-C(c)$
CC (iso to iso-C)	$C-C(d)$
CC (t to t-C)	$C-C(e)$
CC (t to iso-C)	$C-C(f)$

Table 15.190. The geometrical bond parameters of nitroalkanes and experimental values [1].

Parameter	NO ₂ Group	C-N Group	C-H (C ₁ H ₃) Group	C-H (C ₂ H ₅) Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
α (°)	1.3221	1.97794	1.64920	1.67122	2.12499	2.12499	2.10725	2.10725	2.10725	2.10725
α' (°)	1.1421	1.40639	1.04836	1.05553	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length										
2c (Å)	1.22157	1.48846	1.10974	1.11713	1.50280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length	1.224 (nitromethane)	1.489 (nitromethane)	1.107 (C-H propane)	1.117 (C-H propane)	1.532 (propane)	1.532 (propane)	1.531 (propane)	1.532 (propane)	1.531 (propane)	1.531 (propane)
(Å)			1.117 (C-H butane)	1.117 (C-H butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)
λ (°)	0.66526	1.39079	1.27295	1.29569	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
σ	0.60339	0.71104	0.63380	0.63159	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.191. The MO to HO intercept geometrical bond parameters of nitroalkanes. R, P, R' are H or alkyl groups. E_p is $E_p(\text{atom} - \text{atom}, \text{m.u.}, \text{AO})$.

Bond	Atom	E_p (eV) Bond 1	E_p (eV) Bond 2	E_p (eV) Bond 3	E_p (eV) Bond 4	Final Total Energy C2sp ² (eV)	r_{calc} (a ₀)	r_{exp} (a ₀)	E_{calc} (eV) Final	E_{exp} (eV) Final	θ' (°)	θ_i (°)	θ_e (°)	d_i (a ₀)	d_e (a ₀)	d_i (a ₀)
$\text{RNO}_2 = \text{O}$	O	-0.92018	0	0	0	-15.74709	1.80000	0.80359	-15.74709	-15.74709	135.25	44.25	66.05	0.61333	0.61333	0.61333
$\text{RNO}_2 = \text{O}$	N	-0.92018	-0.92018	-0.72457	0	-17.40869	0.92004	0.78155	-17.40869	-17.40869	131.57	46.45	61.50	0.63558	0.63558	0.63558
$\text{H}_2\text{C}-\text{NO}_2$	C	-0.72457	0	0	0	-15.53033	0.91771	0.87505	-15.53033	-15.53033	80.47	99.53	38.35	1.51125	1.51125	1.51125
$\text{H}_2\text{C}-\text{NO}_2$	N	-0.92018	-0.92018	-0.72457	0	-17.40869	0.92004	0.78155	-17.40869	-17.40869	69.20	110.70	31.71	1.60259	1.60259	1.60259
$\text{H}_2\text{C}-\text{NO}_2$	C	-0.72457	-0.92018	0	0	-15.53033	0.91771	0.87505	-15.53033	-15.53033	74.96	105.04	34.99	1.62661	1.62661	1.62661
$\text{C}-\text{H}(\text{CH}_3)$	C	-0.92018	0	0	0	-15.54487	0.91771	0.80359	-15.54487	-15.54487	77.40	102.51	41.48	1.23564	1.23564	1.23564
$\text{C}-\text{H}(\text{CH}_3)$	C	-0.92018	-0.92018	0	0	-15.54706	0.91771	0.81540	-15.54706	-15.54706	68.47	111.53	35.34	1.35486	1.35486	1.35486
$\text{C}-\text{H}(\text{CH}_3)$	C	-0.92018	-0.92018	-0.92018	0	-15.44034	0.91771	0.77247	-15.44034	-15.44034	61.10	118.90	31.37	1.47984	1.47984	1.47984
$\text{H}_2\text{C}-\text{H}_2\text{C}-\text{H}_2$	C	-0.92018	0	0	0	-15.54487	0.91771	0.80359	-15.54487	-15.54487	61.82	116.18	30.08	1.31879	1.31879	1.31879
$\text{H}_2\text{C}-\text{H}_2\text{C}-\text{H}_2$	C	-0.92018	-0.92018	0	0	-15.47405	0.91771	0.81540	-15.47405	-15.47405	58.41	125.59	26.06	1.90830	1.90830	1.90830
$\text{H}_2\text{C}-\text{H}_2\text{C}-\text{H}_2$	C	-0.92018	-0.92018	-0.92018	0	-15.44034	0.91771	0.77247	-15.44034	-15.44034	48.30	131.70	21.90	1.97162	1.97162	1.97162
$\text{H}_2\text{C}-\text{H}_2\text{C}-\text{H}_2$	C	-0.92018	-0.72457	-0.72457	-0.72457	-15.47160	0.91771	0.73889	-15.47160	-15.47160	48.21	131.79	21.74	1.99724	1.99724	1.99724
$\text{H}_2\text{C}-\text{H}_2\text{C}-\text{H}_2$	C	-0.92018	-0.92018	-0.92018	0	-15.44034	0.91771	0.77247	-15.44034	-15.44034	48.20	131.70	21.90	1.97162	1.97162	1.97162
$\text{H}_2\text{C}-\text{H}_2\text{C}-\text{H}_2$	C	-0.92018	-0.72457	-0.72457	-0.72457	-15.45139	0.91771	0.76765	-15.45139	-15.45139	50.04	129.96	22.66	1.94462	1.94462	1.94462
$\text{H}_2\text{C}-\text{H}_2\text{C}-\text{H}_2$	C	-0.72457	-0.92018	-0.92018	0	-15.41963	0.91771	0.78155	-15.41963	-15.41963	52.78	127.22	24.04	1.92443	1.92443	1.92443
$\text{H}_2\text{C}-\text{H}_2\text{C}-\text{H}_2$	C	-0.72457	-0.92018	-0.92018	-0.72457	-15.41963	0.91771	0.76765	-15.41963	-15.41963	50.04	129.96	22.66	1.94462	1.94462	1.94462

Table 15.94. The bond angle parameters of nitroalkanes and experimental values [1]. In the calculation of θ_i , the parameters from the preceding angle were used. $E_i = E_i(\text{atom}, \text{exp. AO})$.

Formula of Anion	$2p^1$ Bond 1 (σ_b)	$2p^1$ Bond 2 (σ_b)	$2p^1$ Terminal Atom (σ_b)	$E_{\text{ionization}}$ of E^- Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{\text{ionization}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	ζ_2 Atom 1	ζ_1 Atom 2	ζ_1 ...	ζ_2	θ_1 ($^\circ$)	θ_2 ($^\circ$)	Calc. θ ($^\circ$)	Exp. θ ($^\circ$)
ZnC_2H	2.09711	2.09711	3.9665	-14.82375 O_h	I	-14.52414	N	0.91771	0.91140 (Eq. 11.1.6b)	0.75	0.99112			106.87	107 (nitromethane)
Zr_2NiO_2	2.20843	2.20843	4.1231	-16.68411 O_h	24	-16.68411 O_h	24	0.81549	0.81549	I	0.81549			126.52	123.3 (nitromethane)
ZrHC_2H Methyl case	2.11106	2.11106	3.4252	-15.75405	7	H	H	0.86559	I	I	1.15796			108.44	107 (propane)
$\text{Zr}_2\text{C}_2\text{C}_2$														112	112 (propane)
$\text{ZrC}_2\text{C}_2\text{H}$												69.51		110.49	113.8 (nitroethane)
Methyl ZrHC_2H	2.09711	2.09711	3.4252	-15.75405	7	H	H	0.86559	I	I	1.15796			110.49	111.4 (nitroethane)
$\text{Zr}_2\text{C}_2\text{C}_2$														111.0	111.0 (nitroethane)
$\text{ZrC}_2\text{C}_2\text{C}_2$														111.4	111.4 (nitroethane)
$\text{ZrC}_2\text{C}_2\text{C}_2$ low C_{2v}	2.01547	2.01547	4.7058	-16.68412 C_h	25	-16.68412 C_h	25	0.81549	0.81549	I	0.81549			109.44	
$\text{ZrC}_2\text{C}_2\text{H}$ low C_{2v}	2.01547	2.11223	4.1633	-15.5033 C_h	5	-14.82375 C_h	I	0.74905	0.91771	I	0.81549			110.67	110.6 (nitroethane)
$\text{ZrC}_2\text{C}_2\text{H}$ low C_{2v}	2.01547	2.09711	4.1633	-15.5033 C_h	5	-14.82375 C_h	I	0.74905	0.91771	I	1.04887			110.76	
$\text{ZrC}_2\text{C}_2\text{C}_2$ low C_{2v}	2.01547	2.09711	4.1633	-15.5033 C_h	5	-14.82375 C_h	I	0.74905	0.91771	I	1.04887			111.27	111.4 (nitroethane)
$\text{ZrC}_2\text{C}_2\text{C}_2$ low C_{2v}	2.00327	2.00327	4.7058	-15.5033 C_h	5	-14.82375 C_h	I	0.74905	0.91771	I	1.04887			111.37	111.4 (nitroethane)
$\text{ZrC}_2\text{C}_2\text{C}_2$												72.50		107.50	

ALKYL NITRITES ($C_nH_{2n+2-m}(NO_2)_m$, $n=1,2,3,4,5\ldots\infty$)

The alkyl nitrites, $C_nH_{2n+2-m}(NO_2)_m$, comprise a $RC-O-NO$ moiety that comprises $C-O$, $O-N$, and NO functional groups. The alkyl portion of the alkyl nitrite may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise 5 methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n -alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t -butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t -butyl, 10 and t -butyl to t -butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrites are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^22s^22p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state 3P_2 . The electron configuration of nitrogen is $1s^22s^22p^3$, and the orbital arrangement given by Eq. (10.134) has 15 three unpaired electrons corresponding to the ground state $^4S_{3/2}$. The bonding in the nitro (NO) functional group is similar to that in the SO group given previously. It also has similarities to the bonding in the carbonyl functional group. In the NO group, the two unpaired electrons of the O atom form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a double bond. The nitrogen atom is then energy matched to the $O-N$ functional 20 group that is further energy matched to the $C2sp^3$ HO of the $C-O$ functional group. To meet the equipotential condition of the union of the $N=O$ H_2 -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.51) for the $N=O$ -bond MO given by Eq. (15.140) is $c_2(O \text{ to } N2p \text{ to } C2sp^3HO) = 0.85987$.

As in the case of the carbonyl group, two unpaired O electrons result upon bond 25 breakage of the $N=O$ bond which requires that two times E_{nog} of oxygen (Eq. (15.59)) be subtracted from the total energy of NO . Additionally, $E_T(atom-atom,msp^3.AO)$ and $\Delta E_{H,MO}(AO/HO)$ are equal to -0.92918 eV (Eq. (14.513)) which matches the energy of the $N=O$ bond with the contiguous $O-N$ bond and matches the energy contribution of an oxygen atom.

The $O-N$ functional group comprise a single-bond, H_2 -type-ellipsoidal-MO between the remaining unpaired nitrogen electron and an unpaired electron of the second oxygen atom which further forms a single bond with the $C2sp^3$ HO of the $C-O$ functional group. In alkyl nitrites, the hybridization factor c_2 of Eq. (15.52) for the $C-O$ -bond MO given by Eq. 5 (15.114) is $c_2(C2sp^3HO \text{ to } O) = 0.85395$. The hybridization factor c_2 of Eq. (15.52) for a $C-N$ -bond MO given by Eq. (15.116) is $c_2(C2sp^3HO \text{ to } N) = 0.91140$. Thus, the hybridization factor c_2 of Eq. (15.52) for $O-N$ that bridges the $C-O$ and $N=O$ bonds given by Eq. (15.69) is

$$c_2(N2p \text{ to } O2p) = \frac{c_2(C2sp^3HO \text{ to } N)}{c_2(C2sp^3HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727 \quad (15.141)$$

10 $E_r(atom - atom, msp^3 AO) = -0.92918 \text{ eV}$ in order to match the energy of the NO group and $E(AO / HO) = -15.35946 \text{ eV}$ in order to match the $C-O$ functional group.

The $C-O$ functional group is equivalent to that of an ether as given in the corresponding section except that $E_r(atom - atom, msp^3 AO)$ and $\Delta E_{H_2MO}(AO / HO)$ are both -0.72457 eV which matches the energy contribution of an independent $C2sp^3$ HO (Eq. 15 (14.151)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrite.

The symbols of the functional groups of branched-chain alkyl nitrites are given in Table 15.195. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrites are given in Tables 20 15.196, 15.197, and 15.198, respectively. The total energy of each alkyl nitrite given in Table 15.199 was calculated as the sum over the integer multiple of each $E_D(group)$ of Table 15.198 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrites determined using Eqs. (15.79-15.108) are given in Table 15.200.

Table 15.195. The symbols of functional groups of alkyl nitrates.

Functional Group	Group Symbol	M _r
NO group		
O-N	O-N	
C-O	C-O	
CH ₃ group	C-H (CH ₃)	
CH ₂ group	C-H (CH ₂)	
CH	C-H	
CC bond (n-C)	C-C (a)	
CC bond (iso-C)	C-C (b)	
CC bond (tert-C)	C-C (c)	
CC (far to iso-C)	C-C (d)	
CC (to i-C)	C-C (e)	
CC (to iso-C)	C-C (f)	

Table 15.196. The geometrical bond parameters of alkyl nitrates and experimental values [1].

Parameter	NO Group	O-N Group	C-O Group	C-H (CH ₃) Group	C-H (CH ₂) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
σ (Å)	1.37255	1.76440	1.83327	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
σ' (Å)	1.15002	1.32831	1.36135	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length												
$2\sigma'$ (Å)	1.21713	1.40582	1.44079	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Expo. Bond Length (Å)	1.205 (methyl nitrate)	1.402 (methyl nitrate)	1.437 (methyl nitrate)	1.107 (C-H propane)	1.107 (C-H propane)	1.122 (isobutane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)
h, σ' (Å)	0.65314 (HNO ₂)	1.432 (HNO ₂)	1.23751	1.117 (C-H butane)	1.117 (C-H butane)	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
σ	0.86955	0.75784	0.73457	0.63180	0.63139	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 13.197. The MO to HO intercept geometrical bond parameters of allyl nitriles. R_1, R_2, R_3 are H or alkyl groups. E_p is $E_p(\text{atom} - \text{atom}, \text{mwp}, \text{AO})$.

Bond	Atom	ΔE_p (eV) Bond 1	E_p (eV) Bond 2	E_p (eV) Bond 3	E_p (eV) Bond 4	Final Total Energy (eV)	r_{mwp} (a.u.)	r_{mwp} (a.u.)	E_{mwp} (eV) Final	δ (2ap) (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a.u.)	d_2 (a.u.)
$RON=O$	O	-0.46459	0	0	0	-15.30234	0.88993	0.88993	-15.30234		127.15	42.85	47.50	0.49764	0.63218
$RON=O$	N	-0.46459	-0.46459	0	0	-15.30234	0.88993	0.88993	-15.30234		126.09	43.91	46.48	0.52181	0.62221
$RO_2=NO_2$	O ₂	-0.46459	-0.36219	0	0	-15.30234	0.88993	0.88993	-15.30234		99.22	80.78	47.63	1.18965	0.13925
$RO_2=NO_2$	N	-0.46459	-0.46459	0	0	-15.30234	0.88993	0.88993	-15.30234		98.76	81.22	47.30	1.19655	0.13175
$RH_2C_2=O_2NO_2$	O ₂	-0.46459	-0.46459	0	0	-15.30234	0.88993	0.88993	-15.30234		91.43	84.57	43.71	1.33962	0.62173
$RH_2C_2=O_2NO_2$	N	-0.46459	-0.46459	0	0	-15.30234	0.88993	0.88993	-15.30234		93.71	86.29	43.31	1.30242	0.57593
$-CH_2H_2C_2=O_2NO_2$	C ₁	-0.36219	-0.36219	0	0	-15.30234	0.88993	0.88993	-15.30234		89.16	90.84	42.16	1.37772	0.01228
$C'-H(CH_2)$	C'	-0.92918	0	0	0	-15.30234	0.88993	0.88993	-15.30234		77.49	102.51	41.48	1.23564	0.14708
$C'-H(CH_2)$	C'	-0.92918	-0.92918	0	0	-15.30234	0.88993	0.88993	-15.30234		68.47	111.53	35.84	1.35416	0.29973
$C'-H(CH_2)$	C'	-0.92918	-0.92918	-0.92918	0	-15.30234	0.88993	0.88993	-15.30234		61.10	118.90	31.37	1.42918	0.37316
$H_2C_2H_2C_2H_2=$	C ₁	-0.92918	0	0	0	-15.30234	0.88993	0.88993	-15.30234		63.82	116.18	30.08	1.83879	0.38106
$H_2C_2H_2C_2H_2=$	C ₁	-0.92918	-0.92918	0	0	-15.30234	0.88993	0.88993	-15.30234		56.41	123.59	26.66	1.90190	0.45117
$H_2C_2H_2C_2H_2=$	C ₁	-0.92918	-0.92918	-0.92918	0	-15.30234	0.88993	0.88993	-15.30234		48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_2H_2C_2H_2=$	C ₁	-0.92918	-0.72457	-0.72457	-0.72457	-15.30234	0.88993	0.88993	-15.30234		48.21	131.79	21.74	1.95734	0.50570
$R-H_2C_2H_2C_2H_2=$	C ₁	-0.92918	-0.72457	-0.72457	0	-15.30234	0.88993	0.88993	-15.30234		48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_2H_2C_2H_2=$	C ₁	-0.92918	-0.72457	-0.72457	-0.72457	-15.30234	0.88993	0.88993	-15.30234		50.04	129.96	22.66	1.94462	0.49298
$R-H_2C_2H_2C_2H_2=$	C ₁	-0.92918	-0.72457	-0.72457	0	-15.30234	0.88993	0.88993	-15.30234		52.76	127.22	24.04	1.97443	0.47279
$R-H_2C_2H_2C_2H_2=$	C ₁	-0.92918	-0.72457	-0.72457	-0.72457	-15.30234	0.88993	0.88993	-15.30234		50.04	129.96	22.66	1.94462	0.49298

Table 15.198. The energy parameters (eV) of functional groups of alkyl nitriles.

Parameters	NO Group	O-N Group	C=O Group	CH ₃ Group	CH ₂ Group	CH Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
η_1	2	1	1	3	2	1	1	1	1	1	1	1	1
η_2	0	0	0	2	1	0	0	0	0	0	0	0	0
η_3	0	0	0	0	0	0	0	0	0	0	0	0	0
ζ_1	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
ζ_2	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_3	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_4	0.5987	1.06727	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
ζ_5	2	0	0	0	1	1	1	0	0	1	1	1	0
ζ_6	4	2	2	1	1	1	1	2	2	2	2	2	2
ζ_7	0	0	0	3	2	1	1	0	0	0	0	0	0
ζ_8	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
ζ_9	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{10}	1	1	1	1	1	1	1	1	1	1	1	1	1
ζ_{11}	-108.34117	-42.83043	-52.04173	-107.52728	-70.41425	-35.12015	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214
ζ_{12}	23.66182	20.48593	9.99436	38.92728	23.78002	12.87680	9.33552	9.33552	9.33552	9.33552	9.33552	9.33552	9.33552
ζ_{13}	40.59520	12.13729	8.64455	32.53914	21.06575	10.48382	6.77464	6.77464	6.77464	6.77464	6.77464	6.77464	6.77464
ζ_{14}	-20.47960	-6.04870	-4.32232	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732
ζ_{15}	0	-15.35946	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{\text{HOMO}} [10^3 \text{ kcal/mol}]$	-0.92918	0	-0.72457	0	0	0	0	0	0	0	0	0	0
$E_{\text{HOMO}} [eV]$	0.92918	-15.35946	-13.91032	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E_{\text{LUMO}} [eV]$	-63.27057	-31.63327	-31.63327	-47.69451	-49.66493	-31.63327	-31.63327	-31.63327	-31.63327	-31.63327	-31.63327	-31.63327	-31.63327
$E_{\text{HOMO}} - E_{\text{LUMO}} [eV]$	-0.92918	-0.92918	-0.72457	0	0	0	0	0	0	0	0	0	0
$E_{\text{HOMO}} - E_{\text{LUMO}} [10^3 \text{ kcal/mol}]$	-64.19992	-32.56455	-32.35994	-67.69450	-49.66493	-31.63327	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373
$\alpha [10^3 \text{ kcal/mol}]$	19.21090	23.3578	20.7201	24.9286	24.2751	24.1759	9.43699	6.21159	6.21159	6.21159	6.21159	6.21159	6.21159
$E_{\text{HOMO}} [eV]$	12.65039	13.37450	13.6490	16.40846	15.97831	15.91299	9.43699	6.21159	6.21159	6.21159	6.21159	6.21159	6.21159
$E_{\text{LUMO}} [eV]$	-0.22587	0.25261	-0.23648	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.16515	-0.16515	-0.16515	-0.16515	-0.16515
$E_{\text{HOMO}} - E_{\text{LUMO}} [eV]$	0.20396	0.10725	0.13663	0.35532	0.35532	0.35532	0.35532	0.35532	0.35532	0.35532	0.35532	0.35532	0.35532
$E_{\text{HOMO}} - E_{\text{LUMO}} [10^3 \text{ kcal/mol}]$	1461	1471	1471	1471	1471	1471	1471	1471	1471	1471	1471	1471	1471
$E_{\text{HOMO}} [eV]$	-0.12390	0.19899	-0.16817	-0.22757	-0.14502	-0.07200	-0.10359	-0.07200	-0.07200	-0.07200	-0.07200	-0.07200	-0.07200
$E_{\text{HOMO}} [eV]$	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\text{HOMO}} - E_{\text{LUMO}} [eV]$	-64.44771	32.76354	-32.52811	-47.92207	-49.60996	-31.70737	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732
$E_{\text{HOMO}} - E_{\text{LUMO}} [10^3 \text{ kcal/mol}]$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{\text{HOMO}} [eV]$	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{\text{HOMO}} [eV]$	5.67933	3.49376	3.25833	12.49186	7.83016	3.32601	4.32754	4.29921	4.29921	4.29921	4.29921	4.29921	4.29921

Table 15.199. The total bond energies of alkyl nitriles calculated using the functional group composition and the energies of Table 15.198 compared to the experimental values [3].

Formula	Name	CH ₃	CH ₂	CH	C-H	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	Calculated Total Bond Energy (kJ/mol)	Experimental Total Bond Energy (kJ/mol)	Relative Error
CH ₃ NO ₂	Methyl nitrite	1	0	0	0	0	0	0	0	0	0	24.9321	24.933	0.0016

ALKYL NITRITES ($C_nH_{2n+2-m}(NO_2)_m$, $n=1,2,3,4,5\ldots\infty$)

The alkyl nitrites, $C_nH_{2n+2-m}(NO_2)_m$, comprise a $RC-O-NO$ moiety that comprises $C-O$, $O-N$, and NO functional groups. The alkyl portion of the alkyl nitrite may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise 5 methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, 10 and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrites are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^22s^22p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state 3P_2 . The electron configuration of nitrogen is $1s^22s^22p^3$, and the orbital arrangement given by Eq. (10.134) has 15 three unpaired electrons corresponding to the ground state $^4S_{3/2}$. The bonding in the nitro (NO) functional group is similar to that in the SO group given previously. It also has similarities to the bonding in the carbonyl functional group. In the NO group, the two unpaired electrons of the O atom form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a double bond. The nitrogen atom is then energy matched to the $O-N$ functional 20 group that is further energy matched to the $C2sp^3$ HO of the $C-O$ functional group. To meet the equipotential condition of the union of the $N=O$ H_2 -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.51) for the $N=O$ -bond MO given by Eq. (15.140) is $c_2(O \text{ to } N2p \text{ to } C2sp^3HO) = 0.85987$.

As in the case of the carbonyl group, two unpaired O electrons result upon bond 25 breakage of the $N=O$ bond which requires that two times E_{mag} of oxygen (Eq. (15.59)) be subtracted from the total energy of NO . Additionally, $E_r(atom-atom,msp^3.AO)$ and $\Delta E_{H_1MO}(AO/HO)$ are equal to -0.92918 eV (Eq. (14.513)) which matches the energy of the $N=O$ bond with the contiguous $O-N$ bond and matches the energy contribution of an oxygen atom.

The $O-N$ functional group comprise a single-bond, H_2 -type-ellipsoidal-MO between the remaining unpaired nitrogen electron and an unpaired electron of the second oxygen atom which further forms a single bond with the $C2sp^3$ HO of the $C-O$ functional group. In alkyl nitrites, the hybridization factor c_2 of Eq. (15.52) for the $C-O$ -bond MO given by Eq. 5 (15.114) is $c_2(C2sp^3HO \text{ to } O) = 0.85395$. The hybridization factor c_2 of Eq. (15.52) for a $C-N$ -bond MO given by Eq. (15.116) is $c_2(C2sp^3HO \text{ to } N) = 0.91140$. Thus, the hybridization factor c_2 of Eq. (15.52) for $O-N$ that bridges the $C-O$ and $N=O$ bonds given by Eq. (15.69) is

$$c_2(N2p \text{ to } O2p) = \frac{c_2(C2sp^3HO \text{ to } N)}{c_2(C2sp^3HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727 \quad (15.141)$$

10 $E_T(atom - atom, msp^3.AO) = -0.92918 \text{ eV}$ in order to match the energy of the NO group and $E(AO / HO) = -15.35946 \text{ eV}$ in order to match the $C-O$ functional group.

The $C-O$ functional group is equivalent to that of an ether as given in the corresponding section except that $E_T(atom - atom, msp^3.AO)$ and $\Delta E_{H_2MO}(AO / HO)$ are both -0.72457 eV which matches the energy contribution of an independent $C2sp^3$ HO (Eq. 15 (14.151)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrite.

The symbols of the functional groups of branched-chain alkyl nitrites are given in Table 15.195. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrites are given in Tables 20 15.196, 15.197, and 15.198, respectively. The total energy of each alkyl nitrite given in Table 15.199 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.198 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrites determined using Eqs. (15.79-15.108) are given in Table 15.200.

Table 15.195. The symbols of functional groups of alkyl nitriles.

Functional Group	Group Symbol
NO group	NO
O-N	O-N
C-O	C-O
CH ₃ group	C-H (CH ₃)
CH ₂ group	C-H (CH ₂)
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (to n-C)	C-C (e)
CC (to iso-C)	C-C (f)

Table 15.196. The geometrical bond parameters of alkyl nitriles and experimental values [1].

Parameter	NO Group	O-N Group	C-O Group	C-H (CH ₃) Group	C-H (CH ₂) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group	C-C (f) Group
σ (Å)	1.32255	1.76440	1.85327	1.64920	1.67122	1.67465	2.12699	2.12499	2.10725	2.12499	2.10725	2.10725	2.10725
σ' (Å)	1.15002	1.32831	1.36135	1.04856	1.05553	1.02661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164	1.45164
Bond Length	1.21713	1.40582	1.44079	1.10974	1.11713	1.11827	1.54280	1.54380	1.53635	1.54280	1.53635	1.53635	1.53635
Exp. Bond Length (Å)	1.205 (methyl nitrile) 1.2 (HNCN ₂)	1.402 (methyl nitrile) 1.433 (HNCN ₂)	1.437 (methyl nitrile)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
h_c (Å)	0.65314	1.16134	1.23751	1.27985	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750	1.52750
ϵ	0.86955	0.75284	0.72457	0.63580	0.63159	0.63095	0.63600	0.68600	0.68888	0.68600	0.68888	0.68888	0.68888

Table 15.197. The MO to HO intercept geometrical bond parameters of alkyl nitriles. R, R', R'' are H or alkyl groups. E_T is $E_T(\text{atom} - \text{atom}, \text{mp}, \text{Å})$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy (E_T) (eV)	r_{bond} (Å)	r_{atom} (Å)	E_{bond} (eV) Final	θ (°)	θ_1 (°)	θ_2 (°)	d_1 (Å)	d_2 (Å)
$RON=O$	O	-0.6459	0	0	0	-15.3034	1.0000	0.8193	-15.3034	137.15	42.85	67.90	0.4974	0.6328
$RON=O$	N	-0.6459	-0.6459	0	0	-15.3034	0.9304	0.8159	-15.3034	136.09	43.91	66.48	0.5271	0.6221
$RO_2=NO_2$	O	-0.6459	-0.6230	0	0	-15.6363	1.0000	0.8693	-15.6363	99.22	80.78	47.63	1.1809	0.1395
$RO_2=NO_2$	N	-0.6459	-0.6459	0	0	-15.6363	0.9304	0.8659	-15.6363	98.78	81.22	47.20	1.1963	0.1375
$RH_2C_2=O_2NO_2$	O	-0.6230	-0.6459	0	0	-15.6363	1.0000	0.8693	-15.6363	91.43	88.57	43.71	1.3362	0.0217
$RH_2C_2=O_2NO_2$	N	-0.6230	0	0	0	-15.1779	0.9171	0.8932	-15.1779	93.71	86.29	45.31	1.3042	0.0593
$C-H(CH_3)$	C	-0.92918	-0.92918	0	0	-153.00716	0.9171	0.84418	-16.11722	82.16	90.84	42.16	1.3753	0.0128
$C-H(CH_3)$	H	-0.92918	0	0	0	-153.4487	0.9171	0.86359	-15.75493	77.49	102.51	41.48	1.2354	0.1870
$C-H(CH_3)$	C	-0.92918	-0.92918	0	0	-153.47406	0.9171	0.81549	-16.0413	68.47	111.53	38.84	1.3466	0.2993
$C-H(CH_3)$	H	-0.92918	-0.92918	0	0	-154.40324	0.9171	0.77247	-17.61330	61.10	118.90	31.37	1.42018	0.3756
$H_2C_2H_2CH_2=$	C	-0.92918	0	0	0	-152.54487	0.9171	0.86359	-15.75493	63.82	116.18	30.08	1.3379	0.38106
$H_2C_2H_2CH_2=$	H	-0.92918	-0.92918	0	0	-153.47406	0.9171	0.81549	-16.0412	56.41	123.59	26.06	1.50990	0.43117
$(C-C)(C)$	C	-0.92918	-0.92918	0	0	-154.40324	0.9171	0.77247	-17.61330	48.30	131.70	21.90	1.97162	0.51318
$R-H_2C_2(R'-H_2C_2)(R''-H_2C_2)CH_2=$	C	-0.92918	-0.72437	-0.72437	-0.72437	-154.71860	0.9171	0.75899	-17.92866	48.21	131.79	21.74	1.9574	0.50570
$(C-C)(C)$	C	-0.92918	-0.92918	0	0	-154.40324	0.9171	0.77247	-17.61330	48.30	131.70	21.90	1.97162	0.51318
$R-H_2C_2(R'-H_2C_2)(R''-H_2C_2)CH_2=$	C	-0.72437	-0.72437	-0.72437	-0.72437	-154.71860	0.9171	0.75899	-17.92866	50.04	129.96	22.66	1.94462	0.49258
$(C-C)(C)$	C	-0.72437	-0.92918	-0.92918	0	-154.19663	0.9171	0.78155	-17.40860	52.76	127.22	24.04	1.92443	0.47279
$R-H_2C_2(R'-H_2C_2)(R''-H_2C_2)CH_2=$	C	-0.72437	-0.72437	-0.72437	-0.72437	-154.71860	0.9171	0.75899	-17.92866	50.04	129.96	22.66	1.94462	0.49258

Table 15.198. The energy parameters (eV) of functional groups of alkyl nitrites.

[illegible]

Table 15.199. The total bond energies of alkyl nitrites calculated using the functional group composition and the energies of Table 15.198 compared to the experimental values [3].

Formula	Name	O-N	C-O	C-N	CH	CH ₂	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	Calculated Total Bond Enthalpy (kJ/mol)	Experimental Total Bond Enthalpy (kJ/mol)	Relative Error
CH ₃ NO ₂	Methyl nitrate	Group	Group	Group	Group	Group	0	0	0	0	0	24.97124	24.97124	0.00126

ALKYL NITRATES ($C_n H_{2n+2-m} (NO_2)_m$, $n = 1, 2, 3, 4, 5 \dots \infty$)

The alkyl nitrates, $C_n H_{2n+2-m} (NO_2)_m$, comprise a $RC-O-NO_2$ moiety that comprises $C-O$, $O-N$, and NO_2 functional groups. The alkyl portion of the alkyl nitrate may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylene (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2 CH$) and t-butyl ($(CH_3)_3 C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrates are equivalent to those in branched-chain alkanes.

The NO_2 functional group is equivalent to that of nitro alkanes with the exception that $\Delta E_{H_1, MO}(AO/HO)$ as well as $E_r(atom-atom, msp^3.AO)$ is equal to -3.71673 eV in order to match the group energy to that of the contiguous $O-N$ bond. Furthermore, the $O-N$ group with $E_r(atom-atom, msp^3.AO) = -0.92918 \text{ eV}$ is equivalent to that of nitrites as given in the corresponding section.

The $C-O$ functional group is equivalent to that of an ether as given in the corresponding section except that $E_r(atom-atom, msp^3.AO)$ and $\Delta E_{H_1, MO}(AO/HO)$ are both -0.92918 eV which matches the energy contribution of an independent $C2sp^3 HO$ (Eq. (14.513)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrate.

The symbols of the functional groups of branched-chain alkyl nitrates are given in Table 15.201. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrates are given in Tables 15.202, 15.203, and 15.204, respectively. The total energy of each alkyl nitrate given in Table 15.205 was calculated as the sum over the integer multiple of each $E_D(Grp)$ of Table 15.204 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrates determined using Eqs. (15.79-15.108) are given in Table 15.206.

Table 1.5.201. The symbols of functional groups of alkyl nitrates.

Functional Group	Group Symbol
NO ₂ group	NO ₂
O-N	O-N
C-O	C-O
CH ₃ group	C-H (CH ₃)
CH ₂ group	C-H (CH ₂)
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Table 1.5.202. The geometrical bond parameters of alkyl nitrates and experimental values [1].

Parameter	NO ₂ Group	O-N Group	C-O Group	C-H (CH ₃) Group	C-H (CH ₂) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
α (°)	1.29538	1.76440	1.83991	1.69920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
ϵ (°)	1.13815	1.32831	1.35643	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length 2c (Å)	1.20456	1.40582	1.43559	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.205 (methyl nitrate) 1.2 (HNO ₂)	1.402 (methyl nitrate) 1.432 (HNO ₂)	1.437 (methyl nitrate)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
b_{1c} (°)	0.61857	1.16134	1.24312	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
ϵ	0.87862	0.75284	0.73723	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.203. The MO to HO intercepi geometrical bond parameters of alkyl alcohols. R, R', R'' are H or alkyl groups. E_p is $E_p(\text{atom} - \text{atom}, \text{mp}, \text{At})$.

Bond	Atom	E_p (eV) Bond 1	E_p (eV) Bond 2	E_p (eV) Bond 3	E_p (eV) Bond 4	Final Total Energy C-2sp ² (eV)	r_{bond} (a ₀)	r_{bond} (a ₀)	$E(\text{C-2sp}^2)$ (eV) Final	θ (°)	θ_1 (°)	θ_2 (°)	d_1 (a ₀)	d_2 (a ₀)
$RN(O) = O$	O	-0.92918	0	0	0	-15.75493	1.00000	0.86359	-15.75493	138.49	41.51	67.70	0.89144	0.64071
$RN(O) = O$	N	-0.92918	-0.92918	-0.46459	0	-17.14470	0.91084	0.76340	-17.14470	135.60	44.40	63.83	0.57133	0.16682
$RO_2 - N(O)_2$	O ₁	-0.46459	-0.46459	0	0	-15.75493	1.00000	0.86359	-15.75493	98.78	81.22	47.50	1.19635	0.13175
$RO_2 - N(O)_2$	N	-0.46459	-0.92918	-0.92918	0	-17.14470	0.91884	0.76340	-17.14470	92.78	87.22	43.03	1.28978	0.03842
$RH_3C_2 - O_2N(O)_2$ $R = H, \text{alkyl}$	O ₁	-0.46459	-0.46459	0	0	-15.75493	1.00000	0.86359	-15.75493	92.15	87.87	43.96	1.23431	0.03212
$H_3C_2 - O_2N(O)_2$	C ₁	-0.46459	0	0	0	-15.29024	0.91771	0.89943	-15.29024	94.36	85.64	45.54	1.28872	0.68771
$-CH_3H_3C_2 - O_2N(O)_2$	C ₂	-0.46459	-0.92918	0	0	-16.21052	0.91771	0.83885	-16.21052	89.90	90.10	42.44	1.33757	0.00143
$C - H (CH_3)$	C	-0.92918	0	0	0	-15.54487	0.91771	0.86359	-15.54487	77.49	102.51	41.48	1.23564	0.18701
$C - H (CH_3)$	C	-0.92918	-0.92918	0	0	-16.08412	0.91771	0.81549	-16.08412	68.47	111.53	35.84	1.35486	0.29933
$C - H (CH_3)$	C	-0.92918	-0.92918	-0.92918	0	-17.61330	0.91771	0.77247	-17.61330	61.10	118.90	31.37	1.42038	0.27226
$H_3C_2H_3CH_2 -$ $(C - C, (b))$	C ₂	-0.92918	0	0	0	-15.54487	0.91771	0.86359	-15.54487	63.82	116.18	30.08	1.43879	0.38106
$H_3C_2H_3CH_2 -$ $(C - C, (b))$	C ₃	-0.92918	-0.92918	0	0	-16.08412	0.91771	0.81549	-16.08412	56.41	122.59	26.06	1.50890	0.45117
$R - H_3C_2C_2(H_3C_2 - R)HCH_3 -$ $(C - C, (b))$	C ₂	-0.92918	-0.92918	-0.92918	0	-15.44024	0.91771	0.77247	-17.61330	48.30	131.70	21.90	1.57102	0.51388
$R - H_3C_2C_2(R - H_3C_2)C_2(R - H_3C_2)CH_3 -$ $(C - C, (b))$	C ₂	-0.92918	-0.72437	-0.72437	-0.72437	-15.471860	0.91771	0.73889	-17.92866	48.21	131.79	21.74	1.59324	0.50570
$isoC_2C_2(H_3C_2 - R)HCH_3 -$ $(C - C, (b))$	C ₂	-0.92918	-0.92918	-0.92918	0	-15.44024	0.91771	0.77247	-17.61330	48.30	131.70	21.90	1.57102	0.51388
$isoC_2C_2(R - H_3C_2)C_2(R - H_3C_2)CH_3 -$ $(C - C, (b))$	C ₂	-0.72437	-0.72437	-0.72437	-0.72437	-15.451939	0.91771	0.76165	-17.92866	50.04	129.96	22.66	1.94402	0.49258
$isoC_2C_2(H_3C_2 - R)HCH_3 -$ $(C - C, (b))$	C ₃	-0.72437	-0.92918	-0.92918	0	-15.410863	0.91771	0.78155	-17.40869	52.78	127.22	24.64	1.92845	0.47279
$isoC_2C_2(R - H_3C_2)C_2(R - H_3C_2)CH_3 -$ $(C - C, (b))$	C ₃	-0.72437	-0.72437	-0.72437	-0.72437	-15.451939	0.91771	0.76165	-17.92866	50.04	129.96	22.66	1.94402	0.49258

Table 15.204. The energy parameters (eV) of functional groups of alkyl nitrates.

Parameters	NO ₂ Group	O-N Group	C-O Group	CH ₃ Group	CH ₂ Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
n_1	2	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
n_4	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1
C_3	1	1	1	1	1	1	1	1	1	1	1	1
C_4	0.85987	1.06727	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
C_5	0	0	0	0	1	1	0	0	1	1	1	0
C_6	4	2	2	1	1	1	2	2	2	2	2	2
C_7	0	0	0	3	2	1	0	0	0	0	0	0
C_8	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_9	1	1	1	1	1	1	1	1	1	1	1	1
C_{10}	1	1	1	1	1	1	1	1	1	1	1	1
V_1 (eV)	-112.63415	-42.83043	-32.35681	-107.32728	-70.41425	-33.12015	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214
V_2 (eV)	23.90868	20.48593	10.03058	38.97278	25.78002	12.87680	9.33552	9.33552	9.33552	9.33552	9.33552	9.33552
V_3 (eV)	43.47534	12.13759	8.79304	32.53914	21.06675	10.48382	6.77464	6.77464	6.77464	6.77464	6.77464	6.77464
V_4 (eV)	-31.73767	-6.06870	-4.39652	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732
$E_{1,100}^{\text{calc}}$ (eV)	0	-15.35946	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{1,100}^{\text{calc}}$ (eV)	-3.71673	-15.35946	-13.70571	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E_{1,100}^{\text{exp}}$ (eV)	3.71673	-15.35946	-13.70571	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E_{1,100}^{\text{calc}}$ (eV)	-63.27107	-31.63527	-31.63542	-47.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537
$E_{1,100}^{\text{exp}}$ (eV)	-3.71673	-0.92018	-0.92018	0	0	0	-1.83836	-1.83836	-1.83836	-1.83836	-1.83836	-1.83836
$E_{1,100}^{\text{calc}}$ (eV)	-66.98746	-32.56455	-32.56455	-67.69450	-69.66493	-31.63537	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373
ω (10 ⁶ rad/s)	19.8278	23.5578	21.0910	24.9286	24.2751	24.1759	6.21159	6.21159	6.21159	6.21159	6.21159	6.21159
$E_{1,100}^{\text{calc}}$ (eV)	-0.25938	0.23261	-0.24004	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.16515	-0.16515	-0.16515	-0.16515
$E_{1,100}^{\text{exp}}$ (eV)	0.19542	0.10725	0.15663	0.35532	0.35532	0.35532	0.12312	0.12312	0.12312	0.12312	0.12312	0.12312
$E_{1,100}^{\text{calc}}$ (eV)	-0.14267	0.19899	-0.17172	-0.22757	-0.14502	-0.07200	-0.10359	-0.07200	-0.10359	-0.10359	-0.10359	-0.10359
$E_{1,100}^{\text{exp}}$ (eV)	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{1,100}^{\text{calc}}$ (eV)	-67.27281	33.76354	-32.73627	-67.92207	-69.80996	-31.70737	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732
$E_{1,100}^{\text{exp}}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{1,100}^{\text{calc}}$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{1,100}^{\text{exp}}$ (eV)	8.73525	3.49376	3.46649	12.49186	7.83016	3.37601	4.32754	4.29921	4.32754	4.29921	4.32754	4.29921

Table 15.205. The total bond energies of alkyl nitrates calculated using the functional group composition and the energies of Table 15.204 compared to the experimental values [3].

Formula	Name	NO ₂ Group	O-N Group	C-O Group	CH ₃ Group	CH ₂ Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH ₃ NO ₂	Methyl nitrate	1	1	1	1	0	0	0	0	0	0	0	0	28.18526	28.117	-0.00244
C ₂ H ₅ NO ₂	Ethyl nitrate	1	1	1	1	1	0	0	0	0	0	0	0	40.54306	40.396	0.00151
C ₃ H ₇ NO ₂	Propyl nitrate	1	1	1	1	2	0	0	0	0	0	0	0	52.50076	52.550	0.00093
C ₄ H ₉ NO ₂	Isopropyl nitrate	1	1	1	1	3	0	0	0	0	0	0	0	64.60163	64.725	0.00233

CYCLIC AND CONJUGATED ALKENES

$$(C_n H_{2n+2-2m-2c}, n=3,4,5\ldots\infty, m=1,2,3\ldots, c=0 \text{ or } 1)$$

The cyclic and conjugated alkenes are represented by the general formula $C_n H_{2n+2-2m-2c}$, $n=3,4,5\ldots\infty$, $m=1,2,3\ldots$, $c=0$ or 1 where m is the number of double bonds and $c=0$ for a straight-chain alkene and $c=1$ for a cyclic alkene. They have at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. Consider the cyclic and conjugated alkenes 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene, and cyclopentene. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, five distinct $C-C$ functional groups can be identified as given in Table 15.208. The designation of the structure of the groups are shown in Figures 61A-E. In addition, CH_2 of any $-C=CH_2$ moiety is an conjugated alkene functional group. The alkyl portion of the cyclic or conjugated alkene may comprise at least one terminal methyl group (CH_3), and may comprise methylene (CH_2), and methylene (CH) functional groups that are equivalent to those of branched-chain alkanes.

The solution of the functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. The $C-C$ groups are solved in the same manner as those of the branched-chain alkanes given in the corresponding section. For example, the cyclopentene $C_a - C_b$ group is equivalent to the $n-C-C$ alkane group. Many of the corresponding energies of the molecules of this class are similar, and they can be related to one another based on the structure. For example, cyclopentadiene is formed by ring closure of 1,3-pentadiene with the elimination of H from the terminal methyl and methylene groups. Thus, the energy of each of the corresponding carbon-carbon bonds in cyclopentadiene is the same as that in 1,3-pentadiene except that the difference between the energies of the 1,3-pentadiene $C_c - C_d$ and the cyclopentadiene $C_a - C_b$ groups is the magnetic energy (Eq. (15.58)) which is subtracted from the $C_a - C_b$ total bond energy according to Eqs. (13.524-13.527) due to the formation of a CH group from the methylene group.

$E_T(\text{atom-atom}, msp^3, AO)$ of the $C=C$ -bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of ethylene, -2.26759 eV , given by

Eq. (14.247). $E_r(\text{atom} - \text{atom}, msp^3.AO)$ of each $C-C$ -bond MO in Eq. (15.52) is -2.26759 eV or -1.85836 eV based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of alkene, -1.13379 eV (Eq. (14.247)), or methylene, -0.92918 eV (Eq. (14.513)), groups, respectively, that are contiguous with the $C-C$ -bond carbons. In the former case, the total energy of the $C-C$ bond MO is matched to that of the alkane energy in the determination of the bond length. The charge density of $0.5e$ must be donated to the $C-C$ bond in order to match the energy of the adjacent flanking double bonds. This further lowers the total energy of the $C-C$ -bond MO and increases the $C-C$ bond energy. This additional lowering of the $C-C$ -bond energy by additional charge donation over that of an alkane bond due to adjacent double bonds is called *conjugation*.

The symbols of the functional groups of cyclic and conjugated alkenes are given in Table 15.207. The structures of 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene, and cyclopentene are shown in Figures 61A-E, respectively. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of cyclic and conjugated alkenes are given in Tables 15.208, 15.209, and 15.210, respectively. The total energy of each cyclic or conjugated alkenes given in Table 15.211 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.210 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(\text{Group})$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of cyclic and conjugated alkenes determined using Eqs. (15.79-15.108) are given in Table 15.212.

Table 15.207. The symbols of functional groups of cyclic and conjugated alkenes.

Functional Group	Group Symbol
CC double bond	C=C
1,3-butadiene, 1,3-pentadiene C_1-C_2	C'-C' (a)
1,3-cyclopentadiene C_1-C_2	C'-C' (b)
1,3-pentadiene C_2-C_3	C'-C' (c)
cyclopentene C_1-C_2	C'-C' (d)
1,4-pentadiene C_1-C_2	C'-C' (e)
1,3-cyclopentadiene C_2-C_3	C'-C' (f)
cyclopentene C_2-C_3	C'-H (CH_2) (i)
CH ₂ alkenyl group	C'-H (CH_2) (ii)
CH ₃ group	C'-H (CH_3) (iii)
CH ₃ alkyl group	C'-H (CH_3) (iii)
CH	C'-H

Table 15.208. The geometrical bond parameters of cyclic and conjugated alkenes and experimental values [1].

Parameter	C=C Group	C'-C' (a) Group	C'-C' (b) Group	C'-C' (c) Group	C=C (d) Group	C'-C' (e) Group	C'-C' (f) Group	C-H (CH_2) (i) Group	C-H (CH_2) (ii) Group	C-H Group
σ (a_0)	1.4728	1.91256	2.04740	2.04740	2.04740	2.17499	1.64010	1.64920	1.67122	1.67465
σ' (a_0)	1.26661	1.38295	1.43087	1.43087	1.43087	1.43773	1.04566	1.04856	1.03553	1.03661
Bond Length $2c'$ (Å)	1.34052	1.46365	1.51437	1.51437	1.51437	1.54280	1.10698	1.10974	1.11713	1.11827
Exp. Bond Length (Å)	1.349 (1,3-butadiene) 1.342 (1,3-cyclopentadiene) 1.342 (1,3-cyclopentadiene) (cyclopentene)	1.467 (1,3-butadiene) 1.469 (1,3-cyclopentadiene) (1,3-cyclopentadiene)	1.519 (cyclopentene)		1.509 (1,3-cyclopentadiene)	1.546 (cyclopentene)	1.10 (2-methylpropane) 1.108 (avg.) (1,3-butadiene)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)
h, c' (a_0)	0.75055	1.32110	1.46439	1.46439	1.46439	1.54615	1.26354	1.27295	1.29569	1.29924
σ	0.86030	0.77209	0.69887	0.69887	0.69887	0.68600	0.63756	0.63580	0.63159	0.63095

Table 15.210. The energy parameters (eV) of functional groups of cyclic and conjugated alkenes.

Parameters	C=C	C-C	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	C-C (g)	C-C (h)	C-C (i)	C-H	C-H	C-H
n_1	2	1	1	1	1	1	1	1	1	1	1	2	2	1
n_2	0	0	0	0	0	0	0	0	0	0	0	1	1	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75
C_2	0.91771	1	1	1	1	1	1	1	1	1	1	1	1	1
C_3	1	1	1	1	1	1	1	1	1	1	1	1	1	1
C_4	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
C_5	0	0	0	0	0	0	0	0	0	0	0	1	1	1
C_6	4	2	2	2	2	2	2	2	2	2	2	3	3	1
C_7	0	0	0	0	0	0	0	0	0	0	0	2	2	1
C_{10}	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75
C_{12}	0.91771	1	1	1	1	1	1	1	1	1	1	1	1	1
V_1 (eV)	-102.08992	-33.01226	-30.19634	-30.19634	-30.19634	-30.19634	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-70.41425	-70.41425	-35.12015
V_2 (eV)	21.48386	9.83824	9.50874	9.50874	9.50874	9.50874	9.33352	9.33352	9.33352	9.33352	9.33352	38.92728	38.92728	12.87680
V_3 (eV)	34.67062	8.63041	7.37432	7.37432	7.37432	7.37432	6.77464	6.77464	6.77464	6.77464	6.77464	21.06675	21.06675	10.48582
V_4 (eV)	-17.33531	-4.31520	-3.68716	-3.68716	-3.68716	-3.68716	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732	-10.53337	-10.53337	-5.24291
E_{100} (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-14.63489	-14.63489	-14.63489
ΔE_{100} (eV)	0	-1.85836	0	0	0	0	0	0	0	0	0	0	0	0
E_1 (eV)	0	-12.77653	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-14.63489	-14.63489	-14.63489
E_2 (eV)	-63.27075	-31.63534	-31.63534	-31.63534	-31.63534	-31.63534	-31.63534	-31.63534	-31.63534	-31.63534	-31.63534	-49.66493	-49.66493	-31.63534
E_3 (eV)	-2.26759	-2.26759	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836	0	0	0
E_4 (eV)	-65.53833	-33.90295	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-49.66493	-49.66493	-31.63537
ω [10^6 rad/s]	43.0680	11.0522	9.97851	23.3291	23.3291	23.3291	9.43699	9.43699	9.43699	9.43699	9.43699	24.2751	24.2751	24.1759
E_5 (eV)	28.34813	7.27475	6.5803	15.3563	15.3563	15.3563	6.21159	6.21159	6.21159	6.21159	6.21159	16.40846	16.40846	15.91299
E_6 (eV)	-0.34517	-0.18090	-0.16982	-0.25966	-0.25966	-0.25966	-0.16515	-0.16515	-0.16515	-0.16515	-0.16515	-0.25017	-0.25017	-0.24966
E_{100} (eV)	0.17897	0.14829	0.11159	0.11159	0.11159	0.11159	0.12312	0.12312	0.12312	0.12312	0.12312	0.35532	0.35532	0.35532
E_{100} (eV)	-0.25568	-0.10676	-0.11402	-0.20386	-0.20386	-0.20386	-0.10359	-0.10359	-0.10359	-0.10359	-0.10359	-0.14502	-0.14502	-0.07200
E_{100} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E_{100} (eV)	-66.04969	-34.00972	-33.60776	-33.60776	-33.60776	-33.60776	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732	-49.80596	-49.80596	-31.70737
E_{100} (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
E_{100} (eV)	0	0	0	0	0	0	0	0	0	0	0	-13.59844	-13.59844	-13.59844
E_{100} (eV)	7.51014	4.73994	4.33798	4.33798	4.33798	4.33798	4.33798	4.33798	4.33798	4.33798	4.33798	7.83968	7.83968	3.32601

Table 15.211. The total bond energies of cyclic and conjugated alkenes calculated using the functional group composition and the energies of Table 15.210 compared to the experimental values [2]. The magnetic energy E_{mag} that is subtracted from the 5 weighted sum of the E_{100} (eV) values based on composition is given by (15.58).

Formula	Name	C=C	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	C-C (g)	C-C (h)	C-H	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_4	1,3 Butadiene	2	1	1	0	0	0	0	0	0	2	0	42.09159	42.12705	0.00044
C_4H_6	1,3 Pentadiene	2	1	1	0	0	0	0	0	0	0	0	54.40776	54.42484	0.00031
C_4H_6	1,4 Pentadiene	2	0	0	2	0	0	0	0	0	2	0	54.03745	54.11806	0.00149
C_5H_8	1,3 Cyclopentadiene	2	1	0	0	2	0	0	0	0	4	0	49.27432	49.30294	0.00038
C_5H_8	Cyclopentene	1	0	2	0	0	0	0	0	3	2	-1	54.83565	54.86117	0.00047

Table 15.2.12. The bond angle parameters of cyclic and conjugated alkenes and experimental values [1]. In the calculation of θ_i , the parameters from the preceding angle were used. E_T is $E_T(\text{atom} - \text{atom}, \text{exp}, \text{AO})$.

Atoms of Angle	$2\theta_1$ Bond 1 (θ_1)	$2\theta_2$ Bond 2 (θ_2)	$2\theta_3$ Terminal Atoms (θ_3)	$E_{\text{calculated}}$ Atom 1 (θ_1)	Atom 1 Hybridization Designation (Table 15.2.1)	θ_1 Atom 1	θ_2 Atom 2	θ_3 Atom 3	E_T (eV)	θ_1 ($^\circ$)	θ_2 ($^\circ$)	θ_3 ($^\circ$)	Exp. θ ($^\circ$)
$\angle \text{HC}^* \text{H}$ $\text{H}_1 \text{C}^* \text{C}_1 = \text{C}_2$ 1,3-butadiene	2.09132	2.09132	3.4928	-15.91955	9	H	H		0				113.25
$\angle \text{C}_1 \text{C}_2 \text{H}_2$ $\text{H}_1 \text{C}^* \text{C}_1 = \text{C}_2$ 1,3-butadiene										113.25			123.58
$\angle \text{C}_1 \text{C}_2 \text{H}_2$ $\text{H}_1 \text{C}^* \text{C}_1 = \text{C}_2$ 1,3-butadiene	2.53321	2.09132	4.0000	-15.91954	9	C_1	C_2		0				120.9
$\angle \text{C}_1 \text{C}_2 \text{C}_3$ $\text{C}_1 = \text{C}_2 \text{C}_3$ 1,3-butadiene	2.53321	2.76590	4.6004	-16.88873	27	C_1	C_2		-1.85836				124.48
$\angle \text{C}_1 \text{C}_2 \text{C}_3$ $\text{C}_1 = \text{C}_2 \text{C}_3$ 1,3-cyclopentadiene	2.53321	2.76590	4.3012	-17.81791	46	C_1	C_2		-1.85836				108.44
$\angle \text{C}_1 \text{C}_2 \text{C}_3$ $\text{C}_1 = \text{C}_2 \text{C}_3$ 1,3-cyclopentadiene	2.86175	2.53321	4.3818	-17.61330	42	C_1	C_2		-1.85836				108.47
$\angle \text{C}_1 \text{C}_2 \text{C}_3$ $\text{C}_1 = \text{C}_2 \text{C}_3$ 1,3-cyclopentadiene	2.86175	2.86175	4.6099	-17.40869	38	C_1	C_2		-1.85836				102.8
$\angle \text{C}_1 \text{C}_2 \text{C}_3$ $\text{C}_1 = \text{C}_2 \text{C}_3$ 1,3-cyclopentadiene	2.86175	2.53321	4.4372	-17.61330	38	C_1	C_2		-1.85836				110.0
$\angle \text{C}_1 \text{C}_2 \text{C}_3$ $\text{C}_1 = \text{C}_2 \text{C}_3$ 1,3-cyclopentadiene	2.91548	2.86175	4.5166	-17.20408	35	C_1	C_2		-1.85836				102.83
$\angle \text{C}_1 \text{C}_2 \text{C}_3$ $\text{C}_1 = \text{C}_2 \text{C}_3$ 1,3-cyclopentadiene	2.91548	2.91548	4.5326	-17.22408	35	C_1	C_2		-1.85836				104.0

AROMATIC AND HETEROCYCLIC COMPOUNDS

Aromatic and heterocyclic molecules comprise at least one of an aromatic or a cyclic conjugated alkene functional group. The latter was described in the Cyclic and Conjugated Alkenes section. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple H_2 -type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule (C_6H_6) section can be generalized to any aromatic function group(s) of aromatic and heterocyclic compounds.

C_6H_6 can be considered a linear combination of three ethylene molecules wherein a $C-H$ bond of each CH_2 group of $H_2C=CH_2$ is replaced by a $C=C$ bond to form a six-member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule (CH_2CH_2) section. The radius $r_{ethylene, 2sp^3}$ ($0.85252a_0$) of the $C2sp^3$ shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy $E_{Coulomb}(C_{ethylene}, 2sp^3)$ ($-15.95955 eV$) of the outer electron of the $C2sp^3$ shell is given by Eq. (14.245). The energy $E(C_{ethylene}, 2sp^3)$ ($-15.76868 eV$) of the outer electron of the $C2sp^3$ shell is given by Eq. (14.246). $E_r(C=C, 2sp^3)$ ($-1.13380 eV$) (Eq. (14.247), the energy change of each $C2sp^3$ shell with the formation of the $C=C$ -bond MO is given by the difference between $E(C_{ethylene}, 2sp^3)$ and $E(C, 2sp^3)$. C_6H_6 can be solved using the same principles as those used to solve ethylene wherein the $2s$ and $2p$ shells of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each $2sp^3$ HO of each carbon atom initially has four unpaired electrons. Thus, the 6 H atomic orbitals (AOs) of benzene contribute six electrons and the six sp^3 -hybridized carbon atoms contribute twenty-four electrons to form six $C-H$ bonds and six $C=C$ bonds. Each $C-H$ bond has two paired electrons with one donated from the H AO and the other from the $C2sp^3$ HO. Each $C=C$ bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two $C2sp^3$ HOs of the participating carbon atoms. Each $C-H$ and each $C=C$ bond comprises a linear combination

of one and two diatomic H_2 -type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively.

Consider the case where three sets of $C = C$ -bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds
5 comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two $C2sp^3$ HOs and 75% of a H_2 -type ellipsoidal MO divided between the $C2sp^3$ HOs:

$$\left(\begin{array}{l} 3(2 C2sp^3 + 0.75 H_2 MO) \rightarrow 3(C=C)^{4e} - \text{ethylene-type-bond MO} \\ \rightarrow 6(C=C)^{3e} - \text{bond MO of benzene} \end{array} \right) \quad (15.142)$$

- 10 The linear combination of each H_2 -type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution per bond from each $C2sp^3$ HO to the $C = C$ -bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond $C = C$ -bond are determined using Eqs. (15.42) and (15.1-15.5) in a form that are the same equations as those used to determine the same parameters of the $C = C$ -bond MO of ethylene (Eqs. (14.242-
15 14.268)) while matching the boundary conditions of the structure of benzene.

Hybridization with 25% electron donation to each $C = C$ -bond gives rise to the $C_{benzene} 2sp^3$ HO-shell Coulombic energy $E_{Coulomb}(C_{benzene}, 2sp^3)$ given by Eq. (14.245). To meet the equipotential condition of the union of the six $C2sp^3$ HOs, c_2 and C_2 of Eq. (15.42) for the aromatic $C=C$ -bond MO is given by Eq. (15.62) as the ratio of 15.95955 eV, the magnitude of
20 $E_{Coulomb}(C_{benzene}, 2sp^3)$ (Eq. (14.245)), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H (Eq. (1.243)):

$$C_2(benzeneC2sp^3 HO) = c_2(benzeneC2sp^3 HO) = \frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252 \quad (15.143)$$

- The energies of each $C=C$ bond of benzene are also determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333) with the parameters of
25 benzene. Ethylene serves as a basis element for the $C=C$ bonding of benzene wherein each of the six $C=C$ bonds of benzene comprises $(0.75)(4) = 3$ electrons according to Eq. (15.142).

The total energy of the bonds of the eighteen electrons of the $C \equiv C$ bonds of benzene, $E_T(C_6H_6, C \equiv C)$, is given by (6)(0.75) times $E_{T+osc}(C \equiv C)$ (Eq. (14.492)), the total energy of the $C \equiv C$ -bond MO of benzene including the Doppler term, minus eighteen times $E(C, 2sp^3)$ (Eq. (14.146)), the initial energy of each $C2sp^3$ HO of each C that forms the $C \equiv C$ bonds of bond order two. Thus, the total energy of the six $C \equiv C$ bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is

$$\begin{aligned} E_T(C_6H_6, C \equiv C) &= (6)(0.75)E_{T+osc}(C \equiv C) - (6)(3)E(C, 2sp^3) \\ &= (6)(0.75)(-66.05796 \text{ eV}) - 18(-14.63489 \text{ eV}) \\ &= -297.26081 \text{ eV} - (-263.42798 \text{ eV}) \\ &= -33.83284 \text{ eV} \end{aligned} \quad (15.144)$$

The results of benzene can be generalized to the class of aromatic and heterocyclic compounds.

E_{hv} of an aromatic bond is given by $E_T(H_2)$ (Eqs. (11.212) and (14.486)), the maximum total energy of each H_2 -type MO such that

$$\bar{E}_{osc} = n_1(\bar{E}_D + \bar{E}_{Kvib}) = n_1 \left(-31.63536831 \text{ eV} \sqrt{\frac{2\bar{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \quad (15.145)$$

The factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two given in the Benzene Molecule (C_6H_6) section modifies Eqs. (15.52-15.56). Multiplication of the total energy given by Eq. (15.55) by $f_1 = 0.75$ with the substitution of Eq. (15.145) gives the total energy of the aromatic bond:

$$E_T(\text{Group}) = f_1 \left(E(\text{basis energies}) + E_T(\text{atom-atom, } msp^3 \text{ AO}) \right. \\ \left. - 31.63536831 \text{ eV} \sqrt{\frac{2\hbar \sqrt{\frac{C_{1a}C_{2a}e^2}{4\pi\epsilon_0 R^3}}}{m_e c^2}} + n_1 \bar{E}_{Kvib} + c_3 \frac{8\pi\mu_a \mu_B^2}{r^3} \right) \quad (15.146)$$

The total bond energy of the aromatic group $E_D(\text{group})$ is the negative difference of the total energy of the group (Eq. (15.146)) and the total energy of the starting species given by the sum of $c_4 E_{\text{initial}}(c_4 \text{ AO} / \text{HO})$ and $c_5 E_{\text{initial}}(c_5 \text{ AO} / \text{HO})$:

$$E_D(\text{group}) = - \left[f_1 \left(\begin{aligned} &E(\text{basis energies}) + E_T(\text{atom} - \text{atom}, \text{msp}^3 \text{ AO}) \\ &- 31.63536831 \text{ eV} \sqrt{\frac{2\hbar^4 \sqrt{\frac{C_{10} C_{20} e^2}{4\pi\epsilon_0 R^3}}}{m_e c^2} + n_1 \bar{E}_{\text{Kub}} + c_3 \frac{8\pi\mu_0 \mu_B^2}{r^3}} \right) - (c_4 E_{\text{initial}}(\text{AO} / \text{HO}) + c_5 E_{\text{initial}}(c_5 \text{ AO} / \text{HO})) \end{aligned} \right) \right] \quad (15.147)$$

5 Since there are three electrons per aromatic bond, c_4 is three times the number of aromatic bonds.

Benzene can also be considered as comprising chemical bonds between six CH radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of CH is given in the Hydrogen Carbide (CH) section. Those of the
10 benzene are given in the Benzene Molecule (C_6H_6) section. The energy components of V_s , V_p , T , V_m , and E_T are the same as those of the hydrogen carbide radical, except that $E_T(\text{C} = \text{C}, 2\text{sp}^3) = -1.13379 \text{ eV}$ (Eq. (14.247)) is subtracted from $E_T(\text{CH})$ of Eq. (13.495) to match the energy of each $\text{C} - \text{H}$ -bond MO to the decrease in the energy of the corresponding $\text{C}2\text{sp}^3 \text{ HO}$. In the corresponding generalization of the aromatic CH group, the geometrical
15 parameters are determined using Eq. (15.42) and Eqs. (15.1-15.5) with $E_T(\text{atom} - \text{atom}, \text{msp}^3 \text{ AO}) = -1.13379 \text{ eV}$.

The total energy of the benzene $\text{C} - \text{H}$ -bond MO, $E_{T_{\text{benzene}}}(\text{C} - \text{H})$, given by Eq. (14.467) is the sum of $0.5E_T(\text{C} = \text{C}, 2\text{sp}^3)$, the energy change of each $\text{C}2\text{sp}^3$ shell per single bond due to the decrease in radius with the formation of the corresponding $\text{C} = \text{C}$ -bond MO (Eq. (14.247)),
20 and $E_{T_{\text{benzene}}}(\text{CH})$, the σ MO contribution given by Eq. (14.441). In the corresponding generalization of the aromatic CH group, the energy parameters are determined using Eqs. (15.146-15.147) with $f_1 = 1$ and $E_T(\text{atom} - \text{atom}, \text{msp}^3 \text{ AO}) = \frac{-1.13379 \text{ eV}}{2}$. Thus, the energy

contribution to the single aromatic CH bond is one half that of the $C=C$ double bond contribution. This matches the energies of the CH and $C=C$ aromatic groups, conserves the electron number with the equivalent charge density as that of $s=1$ in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule. Breakage of the aromatic $C=C$ bonds to 5 give CH groups creates unpaired electrons in these fragments that corresponds to $c_3=1$ in Eq. (15.56) with E_{mag} given by Eq. (15.58).

Each of the $C-H$ bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each $C-H$ bond, $-E_{D_{benzene}}(^{12}CH)$ (Eq. (14.477)), the total energy of the twelve electrons of the six $C-H$ bonds of benzene, $E_T(C_6H_6, C-H)$, given by Eq. (14.494) 10 is

$$E_T(C_6H_6, C-H) = (6) \left(-E_{D_{benzene}}(^{12}CH) \right) = 6(-3.90454 \text{ eV}) = -23.42724 \text{ eV} \quad (15.148)$$

The total bond dissociation energy of benzene, $E_D(C_6H_6)$, given by Eq. (14.495) is the negative sum of $E_T(C_6H_6, C=C)$ (Eq. (14.493)) and $E_T(C_6H_6, C-H)$ (Eq. (14.494)):

$$\begin{aligned} E_D(C_6H_6) &= - \left(E_T(C_6H_6, C=C) + E_T(C_6H_6, C-H) \right) \\ &= - \left((-33.83284 \text{ eV}) + (-23.42724 \text{ eV}) \right) \\ &= 57.2601 \text{ eV} \end{aligned} \quad (15.149)$$

15 Using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)) reproduces the results for benzene given in the Benzene Molecule (C_6H_6) section as shown in Tables 15.214 and 15.216.

The symbols of the functional groups of aromatics and hertocyclics are given in Table 15.213. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and 20 energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aromatics and hertocyclics are given in Tables 15.214, 15.215, and 15.216, respectively. The total energy of benzene given in Table 15.217 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.216 corresponding to functional-group composition of the molecule. The bond angle parameters of benzene determined using Eqs. (15.79-15.108) are given in Table 25 15.218.

Table 15.213. The symbols of functional groups of aromatics and heterocycles.

Functional Group	Group Symbol
CC (aromatic bond)	C=C
CH (aromatic)	C(H) (i)

Table 15.214. The geometrical bond parameters of aromatics and heterocycles and experimental values [1].

Parameter	C=C Group	C(H) Group
σ (Å)	1.47348	1.60061
σ' (Å)	1.31468	1.03299
Bond Length 2 σ' (Å)	1.39140	1.09327
Exp. Bond Length (Å)	1.399 (benzene)	1.101 (benzene)
$h_{\sigma}\sigma'$ (Å)	0.66540	1.22265
σ	0.89223	0.64337

5 Table 15.215. The MO to HO intercept geometrical bond parameters of benzene. E_T is $E_T(\text{atom}, \text{exp}, \text{AO})$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy (eV)	r_{exp} (Å)	r_{calc} (Å)	$E_{\text{calc}}(\text{exp})$ (eV) Final	$E(\text{exp})$ (eV) Final	θ°	θ_1°	θ_2°	d_1 (Å)	d_2 (Å)
C-H (CH)	C	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.43	105.38	38.84	1.24678	0.21379
C=HC=C	C ₂	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.26	45.76	58.98	0.75935	0.55333

Table 15.216. The energy parameters (eV) of functional groups of aromatics and hertocyclics.

Parameters	$C \equiv C$ Group	CH Group
f_1	0.75	1
n_1	2	1
n_2	0	0
n_3	0	0
C_1	0.5	0.75
C_2	0.85252	1
c_1	1	1
c_2	0.85252	0.91771
c_3	0	1
c_4	3	1
c_5	0	1
C_{1o}	0.5	0.75
C_{2o}	0.85252	1
V_e (eV)	-101.12679	-37.10024
V_p (eV)	20.69825	13.17125
T (eV)	34.31559	11.58941
V_m (eV)	-17.15779	-5.79470
E_{AO1HO} (eV)	0	-14.63489
$\Delta E_{H_2MO}(AO1HO)$ (eV)	0	-1.13379
$E_r(AO1HO)$ (eV)	0	-13.50110
$E_r(H_2MO)$ (eV)	-63.27075	-31.63539
$E_r(atom - atom, msp^3.AO)$ (eV)	-2.26759	-0.56690
$E_r(MO)$ (eV)	-65.53833	-32.20226
ω (10^{15} rad / s)	49.7272	26.4826
E_K (eV)	32.73133	17.43132
\bar{E}_D (eV)	-0.35806	-0.26130
\bar{E}_{Kvib} (eV)	0.19649 [49]	0.35532 Eq. (13.458)
\bar{E}_{osc} (eV)	-0.25982	-0.08364
E_{mag} (eV)	0.14803	0.14803
$E_r(Group)$ (eV)	-49.54347	-32.28590
$E_{initial}(c_1 AO1HO)$ (eV)	-14.63489	-14.63489
$E_{initial}(c_3 AO1HO)$ (eV)	0	-13.59844
$E_D(Group)$ (eV)	5.63881	3.90454

Table 15.217. The total bond energies of benzene calculated using the functional group composition and the energies of Table 15.216 compared to the experimental values [2].

Formula	Name	$\text{C}=\text{C}$	$\text{C}-\text{H}$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_6H_6	Benzene	6	6	37.2809	37.28340	0.00006

Table 15.218. The bond angle parameters of benzene and experimental values [1]. E_T is $E_T(\text{atom} - \text{atom}, \text{mp}^2, \text{AO})$.

Atom or Angle	$2s^2$ bond 1 (a_1)	$2s^2$ bond 2 (a_2)	$2s^2$ Total Atom (a_3)	$E_{\text{calculated}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{\text{calculated}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	ζ_1 Atom 1	ζ_2 Atom 2	ζ_3	E_T (eV)	θ_1 ($^\circ$)	θ_2 ($^\circ$)	θ_3 ($^\circ$)	Cal. θ ($^\circ$)	Exp. θ ($^\circ$)
$\angle \text{C}'\text{C}'$ (aromatic)	2.62936	2.62936	4.5595	-17.17218	34	-17.17218	34	0.79232	0.79232		-1.85836				120.19	120 [50-53] (benzene)
$\angle \text{C}'\text{H}$ (aromatic)												120.19			119.91	120 [50-53] (benzene)

NAPHTHALENE

Naphthalene has the formula $C_{10}H_8$ and comprises a planar molecule with two aromatic rings that share a common $C-C$ group. In order to be aromatic, the total number of bonding electrons must be a multiple of 3 since the number of electrons of the aromatic bond is 5 $(0.75)(4)=3$ as shown in the Benzene section. In the case of naphthalene, the peripheral 10 carbons form the aromatic MO with the center bridged by a $C-C$ single bond. Then, 30 electrons of the 48 available form aromatic bonds, two electrons form the bridging $C-C$ single bond, and 16 electrons form the eight $C-H$ single bonds. The energies of the aromatic carbons are given by the same equations as those of benzene (Eqs. (15.42), (15.1-15.5), and 10 (15.146-15.147)), except that there are 10 in naphthalene versus six in benzene. Since there are three electrons per aromatic bond, c_4 is three times ten, the number of aromatic bonds. Similarly, the aromatic $C-H$ group of naphthalene is equivalent to that of benzene.

To meet the equipotential condition of the union of the ten $C2sp^3$ HOs bridged by the $C-C$ single bond, the parameters c_1 , C_2 , and C_{2o} of Eq. (15.42) are one for the $C-C$ group, 15 C_{1o} and C_1 are 0.5, and c_2 given by Eq. (15.142) is $c_2(C2sp^3HO)=0.85252$. Otherwise, the solutions of the $C-C$ bond parameters are equivalent to those of the replaced $C-H$ groups with $E(AO/HO)=-14.63489\text{ eV}$ and $\Delta E_{H,MO}(AO/HO)=-1.13379\text{ eV}$ in Eq. (15.41). Similarly, the energy parameters are determined using Eqs. (15.52-15.56) with

$$E_r(atom-atom,msp^3.AO)=\frac{-1.13379\text{ eV}}{2}.$$

20 The symbols of the functional groups of naphthalene are given in Table 15.219. The corresponding designation of the structure is shown in Figure 62. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of naphthalene are given in Tables 15.220, 15.221, and 15.222, respectively. The total energy of naphthalene given in Table 15.223 was calculated as the sum 25 over the integer multiple of each $E_D(Grp)$ of Table 15.222 corresponding to functional-group composition of the molecule. The bond angle parameters of naphthalene determined using Eqs. (15.79-15.108) are given in Table 15.224.

Table 15.219. The symbols of functional groups of naphthalene.

Functional Group	Group Symbol
C ₁ C ₂ (aromatic bond)	C ₁ C ₂
CH (aromatic)	CH (I)
C ₂ -C ₃ (bridging bond)	C-C

Table 15.220. The geometrical bond parameters of naphthalene and experimental values [1].

Parameter	C ₁ C ₂ Group	CH Group	C-C Group
σ (Å)	1.47348	1.60061	1.75607
c' (Å)	1.31468	1.03299	1.32517
Bond Length Zc' (Å)	1.39140	1.09327	1.40250
Exp. Bond Length (Å)	1.40 (avil.) (naphthalene)	1.101 (benzene)	1.42 (naphthalene)
b, c (Å)	0.66540	1.22265	1.15226
ϵ	0.89223	0.64537	0.73463

Table 15.221. The MO to HO intersept geometrical bond parameters of naphthalene. E_r is $E_r(\text{atom} - \text{atom}, \text{msp}, \text{AO})$.

Bond	Atom	E_r (eV) Bond 1	E_r (eV) Bond 2	E_r (eV) Bond 3	E_r (eV) Bond 4	Final Total Energy C2sp ² (eV)	r_{bond} (Å)	r_{msp} (Å)	$E_{\text{msp}}(\text{C2sp}^2)$ (eV) Final	$E(\text{C2sp}^2)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (Å)	d_2 (Å)
C-H (CH)	C	-0.83035	-0.83035	-0.56690	0	-153.84327	0.91771	0.79397	-17.09334	-16.90248	74.43	105.58	38.84	1.24678	0.21579
C=HC ₂ =C ₃	C ₁	-0.83035	-0.83035	-0.56690	0	-153.84327	0.91771	0.79397	-17.09334	-16.90248	134.34	45.76	58.98	0.75935	0.55533
C=C ₂ (C ₃)=C ₄	C ₁	-0.83035	-0.83035	-0.31345	0	-153.55983	0.91771	0.80599	-16.80989	-16.61903	134.81	45.19	59.66	0.74430	0.57031
$(C_1)_2 C_2 - C_3 - C_4$	C ₁	-0.83035	-0.83035	-0.38365	0	-153.59983	0.91771	0.80599	-16.80989	-16.61903	99.50	80.50	47.66	1.18269	0.14248

Table 15.222. The energy parameters (eV) of functional groups of naphthalene.

Parameters	$\overset{3e}{C=C}$ Group	CH Group	C - C Group
f_1	0.75	1	1
n_1	2	1	1
n_2	0	0	0
n_3	0	0	0
C_1	0.5	0.75	0.5
C_2	0.85252	1	1
c_1	1	1	1
c_2	0.85252	0.91771	0.85252
c_3	0	1	0
c_4	3	1	2
c_5	0	1	0
C_{1o}	0.5	0.75	0.5
C_{2o}	0.85252	1	1
V_o (eV)	-101.12679	-37.10024	-34.43791
V_p (eV)	20.69825	13.17125	10.26723
T (eV)	34.31559	11.58941	9.80539
V_m (eV)	-17.15779	-5.79470	-4.90270
$E(\text{AOIHO})$ (eV)	0	-14.63489	-14.63489
$\Delta E_{H_2MO}(\text{AOIHO})$ (eV)	0	-1.13379	-1.13379
$E_T(\text{AOIHO})$ (eV)	0	-13.50110	-13.50110
$E_T(H_2MO)$ (eV)	-63.27075	-31.63539	-31.63529
$E_T(\text{atom} - \text{atom}, msp^3, AO)$ (eV)	-2.26759	-0.56690	-0.56690
$E_T(MO)$ (eV)	-65.53833	-32.20226	-32.20226
ω (10^{15} rad / s)	49.7272	26.4826	23.6343
E_K (eV)	32.73133	17.43132	15.55648
\bar{E}_D (eV)	-0.35806	-0.26130	-0.25127
\bar{E}_{Kvb} (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.12312 [2]
\bar{E}_{osc} (eV)	-0.25982	-0.08364	-0.18971
E_{mag} (eV)	0.14803	0.14803	0.14803
$E_T(\text{Group})$ (eV)	-49.54347	-32.28590	-32.39198
$E_{initial}(c_1 \text{ AOIHO})$ (eV)	-14.63489	-14.63489	-14.63489
$E_{initial}(c_2 \text{ AOIHO})$ (eV)	0	-13.59844	0
$E_D(\text{Group})$ (eV)	5.63881	3.90454	3.12220

Table 15.223. The total bond energies of naphthalene calculated using the functional group composition and the energies of Table 15.222 compared to the experimental values [2].

Formula	Name	$C \equiv C$	$C=H$	$C-C$	Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_{10}H_8$	Naphthalene	10	8	1		90.74658	90.79145	0.00049

Table 15.224. The bond angle parameters of naphthalene and experimental values [1]. E_r is $E_r(\text{atom} - \text{atom}, \text{msp}^2 \text{AO})$.

Angles of Angle	$2\sigma'$ Bond 1 (α_1)	$2\sigma'$ Bond 2 (α_2)	$2\sigma'$ Terminal Atom (α_3)	E_r Terminal Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	E_r Terminal Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	ζ_1 Atom 1	ζ_2 Atom 2	C_1	C_2	ζ_3	E_r (eV)	θ_1 ($^\circ$)	θ_2 ($^\circ$)	θ_3 ($^\circ$)	Calc. θ ($^\circ$)	Exp. θ ($^\circ$)
$\angle C_1 C_2 C_3$ (naphthalene)	2.62936	2.65016	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1		-1.55836				119.40	119.4 (naphthalene)
$\angle C_1 C_2 H$ (naphthalene)														119.40			120.30	
$\angle C_1 C_2 C_3$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	-1.55816				120.19	120 [50-52] (benzene)
$\angle C_1 C_2 H$ (aromatic)														120.19			120 [50-52] (benzene)	

TOLUENE

Toluene has the formula C_7H_8 and comprises the benzene molecule with one hydrogen atom replaced by a methyl group corresponding to a CH_3 functional group and a $C-C$ functional group. The aromatic $C=C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The CH_3 functional group is the same as that of continuous and branched-chain alkanes given in the corresponding sections.

The bond between the methyl and aromatic ring comprises a $C-C$ functional group that is are solved using the same principles as those used to solve the alkane functional groups wherein the $2s$ and $2p$ AOs of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. To match energies within the MO that bridges methyl and aromatic carbons, $E(AO/HO)$ and $\Delta E_{H,MO}(AO/HO)$ in Eq. (15.41) are -15.35946 eV (Eq. (14.155)) and $\frac{-1.13379 \text{ eV}}{2}$, respectively.

To meet the equipotential condition of the union of the aromatic and methyl $C2sp^3$ HOs of the $C-C$ single bond, the parameters c_1 , C_2 , and C_{2o} of Eq. (15.42) are one for the $C-C$ group, C_{1o} and C_1 are 0.5, and c_2 given by Eq. (13.430) is $c_2(C2sp^3HO) = 0.91771$. To match the energies of the functional groups, $E_r(atom - atom, msp^3.AO)$ of the $C-C$ -bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is -1.13379 eV which is the same energy per $C2sp^3$ HO as that of the replaced $C-H$ group.

The symbols of the functional groups of toluene are given in Table 15.225. The corresponding designation of the structure is shown in Figure 63. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of toluene are given in Tables 15.226, 15.227, and 15.228, respectively. The total energy of toluene given in Table 15.229 was calculated as the sum over the integer multiple of each $E_D(group)$ of Table 15.228 corresponding to functional-group composition of the molecule. The bond angle parameters of toluene determined using Eqs. (15.79-15.108) are given in Table 15.230.

Table 15.225. The symbols of functional groups of toluene.

Functional Group	Group Symbol
CC (aromatic bond)	C=C
CH (aromatic)	C ⁺ H (i)
C'-C ₁ (C ₁ H ₁ to aromatic bond)	C-C'
CH ₃ group	C-H (CH ₃)

Table 15.226. The geometrical bond parameters of toluene and experimental values [1].

Parameter	CH (i) Group	C-C' Group	C-H (CH ₃) Group
σ (Å)	1.47348	2.06004	1.64920
σ' (Å)	1.31468	1.43328	1.04856
Bond Length 2c' (Å)	1.39140	1.09327	1.10974
Exp. Bond Length (Å)	1.399 (toluene)	1.524 (toluene)	1.11 (avg.) (toluene)
$b_{1,2}$ (Å)	0.66540	1.22265	1.47774
σ	0.89223	0.64537	0.69573
			0.63580

Table 15.227. The MO to HO intercept geometrical bond parameters of toluene. E_r is $E_r(\text{atom} - \text{atom}, \text{int}^2, \text{AO})$.

Bond	Atom	E_r (eV) Bond 1	E_r (eV) Bond 2	E_r (eV) Bond 3	E_r (eV) Bond 4	Final Total Energy C2sp ² (eV)	r_{bond} (Å)	$E_{\text{bond}}(\text{C2sp}^2)$ (eV) Final	$E(\text{C2sp}^2)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (Å)	d_2 (Å)
C-H (C ₁ H ₁)	C ₁	-0.16690	0	0	0	-152.18259	0.91771	-15.39265	-15.20178	79.39	101.11	45.13	1.20367	0.15911
C-H (C ₂ H ₂)	C ₂	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
C ₁ =HC ₂ =C ₃	C ₁	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	-17.09334	-16.90248	134.34	45.76	58.58	0.75935	0.55533
C ₂ =HC ₁ =C ₃	C ₂	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	-17.09334	-16.90248	73.38	106.62	34.97	1.68807	0.25279
C ₃ =HC ₁ =C ₂	C ₃	-0.56690	0	0	0	-152.18259	0.91771	-15.39265	-15.20178	61.56	118.44	28.27	1.81430	0.37901
C ₁ -C ₂ -C ₃	C ₁	-0.56690	-0.85035	-0.85035	0	-153.88327	0.91771	-17.09334	-16.90247					

Table 15.228. The energy parameters (eV) of functional groups of toluene.

Parameters	$\overset{3e}{C=C}$ Group	CH (i) Group	C - C Group	CH ₃ Group
f_1	0.75	1		
n_1	2	1	1	3
n_2	0	0	0	2
n_3	0	0	0	0
C_1	0.5	0.75	0.5	0.75
C_2	0.85252	1	1	1
c_1	1	1	1	1
c_2	0.85252	0.91771	0.91771	0.91771
c_3	0	1	0	0
c_4	3	1	2	1
c_5	0	1	0	3
C_{1o}	0.5	0.75	0.5	0.75
C_{2o}	0.85252	1	1	1
V_v (eV)	-101.12679	-37.10024	-29.95792	-107.32728
V_p (eV)	20.69825	13.17125	9.47952	38.92728
T (eV)	34.31559	11.58941	7.27120	32.53914
V_m (eV)	-17.15779	-5.79470	-3.63560	-16.26957
$E_{AO(HO)}$ (eV)	0	-14.63489	-15.35946	-15.56407
ΔE_{H_2MO} (AO(HO)) (eV)	0	-1.13379	-0.56690	0
E_T (AO(HO)) (eV)	0	-13.50110	-14.79257	-15.56407
E_T (H ₂ MO) (eV)	-63.27075	-31.63539	-31.63537	-67.69451
E_T (atom - atom, msp ³ AO) (eV)	-2.26759	-0.56690	-1.13379	0
E_T (MO) (eV)	-65.53833	-32.20226	-32.76916	-67.69450
ω (10 ¹⁵ rad / s)	49.7272	26.4826	16.2731	24.9286
E_K (eV)	32.73133	17.43132	10.71127	16.40846
\bar{E}_D (eV)	-0.35806	-0.26130	-0.21217	-0.25352
\bar{E}_{Kvib} (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.14940 [53]	0.35532 (Eq. (13.458))
\bar{E}_{osc} (eV)	-0.25982	-0.08364	-0.13747	-0.22757
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803
E_T (Group) (eV)	-49.54347	-32.28590	-32.90663	-67.92207
$E_{initial}(e_s, AO(HO))$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(e_s, AO(HO))$ (eV)	0	-13.59844	0	-13.59844
E_D (Group) (eV)	5.63881	3.90454	3.63685	12.49186

Table 15.229. The total bond energies of toluene calculated using the functional group composition and the energies of Table 15.228 compared to the experimental values [7].

Formula	Name	$\text{C}=\text{C}$	CH (I)	C^{H}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_4	Ethylene	6	5	1	69.48425	69.546	0.00083

Table 15.230. The bond angle parameters of toluene and experimental values [1]. E_T is $E_T(\alpha_{\text{ring}} - \alpha_{\text{ring}}, \text{exp}, \text{AO})$.

[illegible]

CHLOROBENZENES

Chlorobenzenes have the formula $C_6H_{6-m}Cl_m$ and comprise the benzene molecule with at least one hydrogen atom replaced by a chlorine atom corresponding to a $C-Cl$ functional group. The aromatic $C=C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section.

The small differences between energies of ortho, meta, and para-dichlorobenzene is due to differences in the energies of vibration in the transition state that contribute to E_{osc} . Two types of $C-Cl$ functional groups can be identified based on symmetry that determine the parameter R in Eq. (15.48). One corresponds to the special case of 1,3,5 substitution and the other corresponds to other cases of single or multiple substitutions of Cl for H . P-dichlorobenzene is representative of the bonding with $R=a$. 1,2,3-trichlorobenzene is the particular case wherein is $R=b$. Also, beyond the binding of three chlorides E_{mag} is subtracted for each additional Cl due to the formation of an unpaired electrons on each $C-Cl$ bond.

The bond between the chlorine and aromatic ring comprises two $C-Cl$ functional groups that are solved using the same principles as those used to solve the alkyl chloride functional groups as given in the corresponding section wherein the $2s$ and $2p$ AOs of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and Cl AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. As in the case of alkyl chlorides, c_2 of Eq. (15.52) for each $C-Cl$ -bond MO is one, and the energy matching condition is determined by the C_2 parameter given by Eq. (15.111) which is $C_2(C2sp^3HO \text{ to } Cl) = 0.81317$. To match energies within the MO that bridges the chlorine AO and aromatic carbon $C2sp^3$ HO, $E(AO/HO)$ and $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.42) are -14.63489 eV and -2.99216 eV , respectively. The latter matches twice that of the replaced $C-H$ -bond MO plus $E_T(atom-atom,msp^3.AO)$. To match the energies of the functional groups, $E_T(atom-atom,msp^3.AO)$ of the $C-Cl$ -bond MO in Eq. (15.53) due to the charge donation from the C and Cl atoms to the MO is -0.72457 eV (Eq. (14.151)).

The symbols of the functional groups of chlorobenzenes are given in Table 15.231. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of chlorobenzenes are given in Tables 15.232, 15.233, and 15.234, respectively. The total energy of each chlorobenzene given in Table 15.235 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.234 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(\text{Group})$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of chlorobenzenes determined using Eqs. (15.79-15.108) are given in Table 15.236.

Table 15.231. The symbols of functional groups of chlorobenzenes.

Functional Group	Group Symbol
CC (aromatic bond)	$C \equiv C$
CH (aromatic)	CH (i)
Cl - C (Cl to aromatic bond)	C - Cl (a)
Cl - C (Cl to aromatic bond of 1,3,5-trichlorobenzene)	C - Cl (b)

Table 15.232. The geometrical bond parameters of chlorobenzenes and experimental values [1]

Parameter	C ⁶ Group	CH (I) Group	C-CI (a) Group	C-CI (b) Group
a (Å)	1.47348	1.60061	2.20799	2.20799
c (Å)	1.31468	1.03299	1.64782	1.64782
Bond Length	1.39140	1.09327	1.74397	1.74397
Exp. Bond Length (Å)	1.400 (chlorobenzene)	1.083 (chlorobenzene)	1.737 (chlorobenzene)	1.737 (chlorobenzene)
A_1 (°)	0.66540	1.22265	1.46967	1.46967
A_2 (°)	0.89223	0.64537	0.74630	0.74630

Table 15.233. The MO to HO intercept geometrical bond parameters of chlorobenzenes. E_f is $E_f(\text{atom} - \text{atom}, \text{exp}, \text{MO})$.

Bond	Atom	E_f (eV)	E_f (eV)	E_f (eV)	E_f (eV)	Final Total Energy (eV)	r_{exp} (Å)	r_{MO} (Å)	$E_{\text{MO}}(\text{C}2p^2)$ (eV)	$E(\text{C}2p^2)$ (eV)	θ^* (°)	θ_1 (°)	θ_2 (°)	d_1 (Å)	d_2 (Å)
C-H (C ₁ H)	C ₁	-0.85035	-0.85035	-0.56690	0	-151.88327	0.91771	0.79597	-17.09334	-16.50248	76.42	105.58	38.84	1.24678	0.21379
C ⁶ =HC ⁶ =C ⁶	C ₆	-0.85035	-0.85035	-0.56690	0	-151.88327	0.91771	0.79597	-17.09334	-16.50248	134.24	45.76	58.98	0.75935	0.55533
C ⁶ =C ⁶ -C ¹	C ₆	-0.85035	-0.85035	-0.85035	0	-151.67867	0.91771	0.80561	-16.88873	-16.69786	72.32	106.68	31.67	1.87911	0.23129
C ⁶ =C ⁶ -C ¹	C ¹	-0.36129	0	0	0		1.05158	0.89382	15.18804		82.92	97.08	37.22	1.75824	0.11042
C ₁ =C ⁶ (C ¹)C ₆ =C ₁	C ₆	-0.36129	-0.85035	-0.85035	0	-151.67867	0.91771	0.80561	-16.88873	-16.69786	134.65	45.35	59.67	0.74854	0.56614

Table 1. The energy parameters (eV) of functional groups of chlorobenzenes.

Parameters	C=C Group	CH (I) Group	C-Cl (a) Group	C-Cl (b) Group
f_1	0.75	1		
n_1	2	1	1	1
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.75	0.5	0.5
C_2	0.85252	1	0.81317	0.81317
c_1	1	1	1	1
c_2	0.85252	0.91771	1	1
c_3	0	1	0	0
c_4	3	1	2	2
c_5	0	1	0	0
C_{10}	0.5	0.75	0.5	0.5
C_{20}	0.85252	1	0.81317	0.81317
V_e (eV)	-101.12679	-37.10024	-31.85648	-31.85648
V_p (eV)	20.69825	13.17125	8.25686	8.25686
T (eV)	34.31559	11.58941	7.21391	7.21391
V_m (eV)	-17.15779	-5.79470	-3.60695	-3.60695
$E(\text{AOIHO})$ (eV)	0	-14.63489	-14.63489	-14.63489
$\Delta E_{H_2MO}(\text{AOIHO})$ (eV)	0	-1.13379	-2.99216	-2.99216
$E_T(\text{AOIHO})$ (eV)	0	-13.50110	-11.64273	-11.64273
$E_T(H_2MO)$ (eV)	-63.27075	-31.63539	-31.63539	-31.63539
$E_T(\text{atom-atom, msp}^3 \cdot \text{AO})$ (eV)	-2.26759	-0.56690	-0.72457	-0.72457
$E_T(MO)$ (eV)	-65.53833	-32.20226	-32.35994	-32.35994
ω (10^{15} rad/s)	49.7272	26.4826	8.03459	14.7956
E_K (eV)	32.73133	17.43132	5.28851	9.73870
\bar{E}_n (eV)	-0.35806	-0.26130	-0.14722	-0.19978
\bar{E}_{Kvb} (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.08059 [12]	0.08059 [12]
\bar{E}_{usr} (eV)	-0.25982	-0.08364	-0.10693	-0.15949
E_{msk} (eV)	0.14803	0.14803	0.14803	0.14803
$E_T(\text{Group})$ (eV)	-49.54347	-32.28590	-32.46687	-32.51943
$E_{inhd}(v_1 \text{ AOIHO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{vibnd}(v_1 \text{ AOIHO})$ (eV)	0	-13.59844	0	0
$E_D(\text{Group})$ (eV)	5.63881	3.90454	3.19709	3.24965

Table 13.235. The total bond energies of chlorobenzenes calculated using the functional group composition and the energies of Table 13.234 compared to the experimental values [2]. The magnetic entropy E_{mag} that is subtracted from the weighted sum of the E_r (kJ/mol) values based on composition is given by (13.58).

Formula	Name	C-C	CH (1)	C-Cl (a)	C-Cl (b)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$\text{C}_6\text{H}_5\text{Cl}$	Chlorobenzene	6	5	1	0	0	55.5285	55.51	0.00031
$\text{C}_6\text{H}_4\text{Cl}_2$	m-dichlorobenzene	6	4	2	0	0	55.4918	55.45	0.00012
$\text{C}_6\text{H}_3\text{Cl}_3$	1,2,3-trichlorobenzene	6	3	3	0	0	55.4518	55.072	-0.00115
$\text{C}_6\text{H}_2\text{Cl}_4$	1,2,3,4-tetrachlorobenzene	6	2	4	0	0	55.3842	55.135	-0.00073
C_6Cl_6	Hexachlorobenzene	6	0	6	0	3	55.57130	55.477	-0.00179

Table 13.236. The bond angle parameters of chlorobenzenes and experimental values [1]. E_r is $E_r(\text{atom} - \text{atom}, \text{mdeg}, \text{AO})$.

Atom of Angle	$2C'$ (bond 1) (α_1)	$2C'$ (bond 3) (α_2)	$2C'$ (bond 4) (α_3)	E_r (bond 1) (atom 1)	Atom 1 Hybridization Designation (Table 13.3.A)	E_r (bond 2) (atom 2)	Atom 2 Hybridization Designation (Table 13.3.A)	α_1 (atom 1)	α_2 (atom 2)	α_3	α_4	α_5	α_6	E_r (eV)	θ_1 (°)	θ_2 (°)	θ_3 (°)	Cal. θ (°)	Exp. θ (°)
$\angle \text{CCC}'$ (aromatic)	2.68936	2.68936	4.5385	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85816				120.19	120.19
$\angle \text{CCH}$ $\angle \text{CCCl}$ (aromatic)															120.19			119.91	120 [50-51] 121.7 chlorobenzene 120 [50-51] (benzene)
$\angle \text{CCH}$ $\angle \text{CCCl}$ (aromatic)																			120 [50-51] (benzene)

PHENOL

Phenol has the formula C_6H_6O and comprises the benzene molecule with one hydrogen atom replaced by a hydroxyl corresponding to an OH functional group and a $C-O$ functional group. The aromatic $C \equiv C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The OH functional group is the same as that of alcohols given in the corresponding section.

The bond between the hydroxyl and aromatic ring comprises a $C-O$ functional group that is are solved using the same principles as those used to solve the alcohol functional groups wherein the $2s$ and $2p$ AOs of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and O AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. In aryl alcohols, the aromatic $C2sp^3$ HO has a hybridization factor of 0.85252 (Eq. (15.143)) with an initial energy of $E(C, 2sp^3) = -14.63489 \text{ eV}$ (Eq. (15.25)) and the O AO has an energy of $E(O) = -13.61806 \text{ eV}$. To meet the equipotential condition of the union of the $C-O$ H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C-O$ -bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(\text{aryl}C2sp^3HO \text{ to } O) &= \frac{E(O)}{E(C, 2sp^3)} c_2(\text{aryl}C2sp^3HO) \\ &= \frac{-13.61806 \text{ eV}}{-14.63489 \text{ eV}} (0.85252) \\ &= 0.79329 \end{aligned} \quad (15.150)$$

$E_r(\text{atom-atom}, msp^3 \text{ AO})$ of the $C-O$ -bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is -1.49608 eV . It is based on the energy match between the OH group and the $C2sp^3$ HO of an aryl group and is given by the linear combination of -0.92918 eV (Eq. (14.513)) and -1.13379 eV (Eq. (14.247)), respectively.

The symbols of the functional groups of phenol are given in Table 15.237. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of phenol are given in Tables 15.238, 15.239, and 15.240, respectively. The total energy of phenol given in Table 15.241 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.240

corresponding to functional-group composition of the molecule. The bond angle parameters of phenol determined using Eqs. (15.79-15.108) are given in Table 15.242.

Table 15.237. The symbols of functional groups of phenol.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{3e}{C=C}$
CH (aromatic)	CH (i)
Aryl C-O	C-O (a)
OH group	OH

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Table 15.238. The geometrical bond parameters of phenol and experimental values [1].

Parameter	$\overset{3e}{C=C}$ Group	CH (i) Group	C-O (a) Group	OH Group
$a (a_0)$	1.47348	1.60061	1.68220	1.26430
$c' (a_0)$	1.31468	1.03299	1.29700	0.91808
Bond Length $2c' (\text{\AA})$	1.39140	1.09327	1.37268	0.971651
Exp. Bond Length (\AA)	1.397 avg. (phenol)	1.084 (phenol)	1.364 (phenol)	0.956 (phenol)
$b, c (a_0)$	0.66540	1.22265	1.07126	0.86925
e	0.89223	0.64537	0.77101	0.72615

Table 13.239. The MO to HO intercept geometrical bond parameters of phenol. E_i is $E_i(\text{atom}, \text{mp}, \text{M})$.

Bond	Atom	E_i (eV)	E_j (eV)	E_k (eV)	E_l (eV)	Final Total Energy (eV)	r_{bond} (Å)	r_{bond} (Å)	$E_{\text{bond}}(2p)$ (eV)	$E(C2p)$ (eV)	θ' (°)	θ (°)	θ_2 (°)	d_1 (Å)	d_2 (Å)
$C-H$ (C,H)	C _H	-0.35035	-0.35035	-0.56690	0	-151.88327	0.91771	0.79397	-17.09334	-16.90248	74.42	105.38	35.84	1.24878	0.21379
$C_2=$ $C_2=O-H$	O	-0.74804	0	0	0		1.00000	0.87363	-15.57379		115.79	64.21	64.83	0.33799	0.38009
$C_2=$ C_2-OH	C _H	-0.74804	-0.35035	-0.35035	0	-154.06442	0.91771	0.78762	-17.27448	-17.08362	100.00	80.00	46.39	1.16026	0.13674
$C_2=$ C_2-OH	O	-0.74804	0	0	0		1.00000	0.87363	15.57379		106.51	73.49	51.43	1.04871	0.24829
$C_2=$ C_2-OH	C _H	-0.74804	-0.35035	-0.35035	0	-154.06442	0.91771	0.78762	-17.27448	-17.08362	133.88	46.12	58.35	0.76670	0.54598
$C_2=$ C_2-OH	O	-0.74804	-0.35035	-0.56690	0	-153.88327	0.91771	0.79397	-17.09334	-16.90248	134.24	45.76	58.98	0.73935	0.55533

Table 15.240. The energy parameters (eV) of functional groups of phenol.

Parameters	$\text{C}=\text{C}$ Group	CH (i) Group	$\text{C}-\text{O}$ (a) Group	OH Group
f_1	0.75	1		
n_1	2	1	1	1
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.75	0.5	0.75
C_2	0.85252	1	1	1
c_1	1	1	1	0.75
c_2	0.85252	0.91771	0.79329	1
c_3	0	1	0	1
c_4	3	1	2	1
c_5	0	1	0	1
C_{1a}	0.5	0.75	0.5	0.75
C_{2a}	0.85252	1	1	1
V_e (eV)	-101.12679	-37.10024	-34.04658	-40.92709
V_p (eV)	20.69825	13.17125	10.49024	14.81988
T (eV)	34.31559	11.58941	10.11966	16.18567
V_m (eV)	-17.15779	-5.79470	-5.05983	-8.09284
$E(\text{AOIHO})$ (eV)	0	-14.63489	-14.63489	-13.6181
$\Delta E_{H_2MO}(\text{AOIHO})$ (eV)	0	-1.13379	-1.49608	0
$E_r(\text{AOIHO})$ (eV)	0	-13.50110	-13.13881	-13.6181
$E_r(H_2MO)$ (eV)	-63.27075	-31.63539	-31.63532	-31.63247
$E_r(\text{atom-atom,msp}^3\text{AO})$ (eV)	-2.26759	-0.56690	-1.49608	0
$E_r(MO)$ (eV)	-65.53833	-32.20226	-33.13145	-31.63537
ω (10^{15} rad/s)	49.7272	26.4826	13.3984	44.1776
E_K (eV)	32.73133	17.43132	8.81907	29.07844
\bar{E}_p (eV)	-0.35806	-0.26130	-0.19465	-0.33749
\bar{E}_{Kvib} (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.12808 [19]	0.46311 [17-18]
\bar{E}_{osc} (eV)	-0.25982	-0.08364	-0.13061	-0.10594
E_{max} (eV)	0.14803	0.14803	0.14803	0.11441
$E_r(\text{group})$ (eV)	-49.54347	-32.28590	-33.26206	-31.74130
$E_{total}(c_1 \text{ AOIHO})$ (eV)	-14.63489	-14.63489	-14.63489	-13.6181
$E_{total}(c_2 \text{ AOIHO})$ (eV)	0	-13.59844	0	-13.59844
$E_D(\text{group})$ (eV)	5.63881	3.90454	3.99228	4.41035

Table 15.241. The total bond energies of phenol calculated using the functional group composition and the energies of Table 15.240 compared to the experimental values [2].

[illegible]

Table 15.242. The bond angle parameters of phenol and experimental values [1]. E_7 is $E_7(\text{center-atom}, \text{map}, \text{AO})$.

Atom of Angle	2C ^a Bond 1 (a ₂)	2C ^b Bond 2 (a ₂)	2C ^c Bond 3 (a ₂)	F _{symmetric} Atom 1	Atom 1 Hybridization Designation	F _{symmetric} Atom 1	Atom 2 Hybridization Designation	ζ ₁ Atom 1	ζ ₂ Atom 2	ζ ₃ Atom 3	ζ ₄ Atom 4	ζ ₅ Atom 5	E _γ (eV)	θ ₁ (°)	θ ₂ (°)	θ ₃ (°)	Col. θ (°)	Exp. θ (°)	
ΔC-C ^a (Bromobenzene)	2.62356	2.62356	-4.5985	-17.17218	3d (Table 15.3.A)	-17.17218	3d (Table 15.3.A)	0.79232	0.79232	1	1	0.79232	-1.85756					120.19	120 [55-52] (benzene)
ΔC-C ^b (Bromobenzene)														170.49				119.51	120 [50-52] (benzene)
ΔC-C ^c (Benzene)	2.59389	1.83016	2.0315	-14.82575	f	-14.82575	f	f	0.91771	0.73	1	-0.73	0.91771	0			100.34	109.0 (benzene)	

ANILINE

Aniline and methyl aniline have the formula C_6H_7N and C_7H_8N , respectively. They comprise the benzene and toluene molecules with one hydrogen atom replaced by an amino group corresponding to an NH_2 functional group and a $C-N$ functional group. The aromatic $C \equiv C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The $C-C$ and CH_3 functional groups of methyl anilines are equivalent to those of toluene given in the corresponding section.

The aryl amino (NH_2) functional group was solved using the procedure given in the Dihydrogen Nitride (NH_2) section. Using the results of Eqs. (13.245-13.368), the aryl amino parameters in Eq. (15.51) are $n_1 = 2$, $C_1 = 0.75$, $C_2 = 0.93613$ (Eqs. (13.248-13.249)), $C_{1o} = 1.5$, and $c_1 = 0.75$. In the determination of the hybridization factor c_2 of Eq. (15.52) for the $N-H$ -bond MO of aryl amines, the $C2sp^3$ HO of the $C-NH_2$ -bond MO has an energy of $E(C, 2sp^3) = -15.76868 \text{ eV}$ (Eq. (15.18) corresponding to $s = 2$ in Eqs. (15.18-15.20), and the N AO has an energy of $E(N) = -14.53414 \text{ eV}$. To meet the equipotential condition of the union of the $N-H$ H_2 -type-ellipsoidal-MO with the $C2sp^3$ HO, the hybridization factor c_2 given by Eq. (15.68) is

$$c_2(H \text{ to aniline } N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.76868 \text{ eV}} = 0.92171 \quad (15.151)$$

The bond between the amino and aromatic ring comprises a $C-N$ functional group that is the same as that of 2° amines (methylene) except that the energies corresponding to oscillation in the transition state are those of aniline. The group is solved using the same principles as those used to solve the primary and secondary-amine functional groups wherein the $2s$ and $2p$ AOs of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and N AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. The hybridization is determined in a similar manner to that of the $C-O$ group of phenol. In anilines, the aromatic $C2sp^3$ HO has a hybridization factor of 0.85252 (Eq. (15.143)) with an initial energy of $E(C, 2sp^3) = -14.63489 \text{ eV}$ (Eq. (15.25)) and the N AO has an energy

of $E(N) = -14.53414 \text{ eV}$. To meet the equipotential condition of the union of the $C-O$ H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.51) for the $C-O$ -bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(\text{aryl}C2sp^3HO \text{ to } N) &= \frac{E(N)}{E(C,2sp^3)} c_2(\text{aryl}C2sp^3HO) \\ &= \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}} (0.85252) \\ &= 0.84665 \end{aligned} \quad (15.152)$$

- 5 $E_T(\text{atom-atom}, msp^3.AO)$ of the $C-N$ -bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is -1.13379 eV (Eq. (14.247)). It is based on the energy match between the NH_2 group and the $C2sp^3$ HO of the aryl group and is twice that of the aryl $C-H$ group that it replaces.
- 10 The symbols of the functional groups of aniline and methyl-substituted anilines are given in Table 15.243. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aniline and methyl-substituted anilines are given in Tables 15.244, 15.245, and 15.246, respectively. The total energy of each aniline and methyl-substituted aniline given in
- 15 Table 15.247 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.246 corresponding to functional-group composition of the molecule. The bond angle parameters of aniline and methyl-substituted anilines determined using Eqs. (15.79-15.108) are given in Table 15.248.

20 Table 15.243. The symbols of functional groups of aniline and methyl-substituted anilines.

Functional Group	Group Symbol
CC (aromatic bond)	$C \equiv C$
CH (aromatic)	CH (i)
Aryl C-N	$C-N$ (a)
NH_2 group	NH_2
C_a-C_b (CH_3 to aromatic bond)	$C-C$ (a)
CH_3 group	$C-H$ (CH_3)

Table 15.244. The geometrical bond parameters of aniline and methyl-substituted anilines and experimental values [1].

Parameter	r_{C-C} (Å)	r_{C-N} (Å)	r_{N-H} (Å)	r_{C-H} (Å)
σ (°)	1.07348	1.00061	1.24428	1.04920
τ (°)	1.31468	1.03299	0.94134	1.04856
Bond Length	1.39140	1.09327	1.42449	1.10974
Exp. Bond Length (phenol) (Å)	1.397 avg.	1.084 (phenol)	0.998 (aniline)	1.11 (avg.) (toluene)
r_{H-C} (Å)	0.66540	1.22165	0.81270	1.47774
r	0.89223	0.64537	0.75653	0.63380

Table 15.245. The MO to HO intercepts geometrical bond parameters of aniline and methyl-substituted anilines. E_r is E_r (atom-atom, mp, Å).

Bond	Atom	E_r (eV) Bond 1	E_r (eV) Bond 2	E_r (eV) Bond 3	E_r (eV) Bond 4	Final Total Energy (eV)	r_{bond} (Å)	r_{bond} (Å)	$E(C_{2sp})$ (eV) Final	θ (°)	θ_1 (°)	θ_2 (°)	d_1 (Å)	d_2 (Å)
$C-H$ (C_1H)	C_1	-0.85035	-0.85035	-0.56690	0	-152.80528	0.91771	0.79397	-17.00334	74.42	102.58	31.84	1.24678	0.21779
$C-H$ (C_2H)	C_2	-0.56690	0	0	0	-152.10239	0.91771	0.83392	-15.39265	79.89	101.11	43.13	1.20367	0.15511
C_1-NH-H	N	-0.56690	0	0	0		0.95084	0.83392	-15.39265	121.74	58.26	67.49	0.47034	0.46508
C_1-NH_2	C_1	-0.56690	-0.85035	-0.85035	0	-153.14328	0.91771	0.79397	-17.00334	88.40	91.51	41.01	1.36696	0.02101
C_1-NH_2	N	-0.56690	0	0	0		0.95084	0.83392	-15.39265	96.33	81.68	46.43	1.24839	0.07726
$C_1-C_2H_2$	C_1	-0.56690	0	0	0	-152.18259	0.91771	0.83392	-15.39265	73.18	106.62	34.97	1.61807	0.22279
$C_1-C_2H_2$	C_2	-0.56690	-0.85035	-0.85035	0	-153.14328	0.91771	0.79397	-17.00334	61.56	118.44	28.37	1.41430	0.37901
$C_1-HC_2=CH_2$	C_1	-0.56690	-0.85035	-0.56690	0	-153.18327	0.91771	0.79397	-17.00334	134.24	43.76	54.98	0.39635	0.55003

Table 15.246. The energy parameters (eV) of functional groups of aniline and methyl-substituted anilines.

Parameters	$\overset{3e}{C=C}$ Group	CH (i) Group	C-N (a) Group	NH ₂ Group	C-C (a) Group	CH ₃ Group
f_1	0.75	1				
η_1	2	1	1	2	1	3
η_2	0	0	0	0	0	2
η_3	0	0	0	1	0	0
C_1	0.5	0.75	0.5	0.75	0.5	0.75
C_2	0.85252	1	1	0.93613	1	1
c_1	1	1	1	0.75	1	1
c_2	0.85252	0.91771	0.84665	0.92171	0.91771	0.91771
c_3	0	1	0	0	0	0
c_4	3	1	2	1	2	1
c_5	0	1	0	2	0	3
C_{1a}	0.5	0.75	0.5	1.5	0.5	0.75
C_{2a}	0.85252	1	1	1	1	1
V_c (eV)	-101.12679	-37.10024	-32.76465	-78.97795	-29.95792	-107.32728
V_p (eV)	20.69825	13.17125	10.10870	28.90735	9.47952	38.92728
T (eV)	34.31559	11.58941	9.04312	31.73641	7.27120	32.53914
V_m (eV)	-17.15779	-5.79470	-4.52156	-15.86820	-3.63560	-16.26957
$E(\text{aonho})$ (eV)	0	-14.63489	-14.63489	-14.53414	-15.35946	-15.56407
$\Delta E_{H_2MO}(\text{aonho})$ (eV)	0	-1.13379	-1.13379	0	-0.56690	0
$E_T(\text{aonho})$ (eV)	0	-13.50110	-13.50110	-14.53414	-14.79257	-15.56407
$E(\pi, \text{aonho})$ (eV)	0	0	0	-14.53414	0	0
$E_T(\pi, MO)$ (eV)	-63.27075	-31.63539	-31.63549	-48.73654	-31.63537	-67.69451
$E_T(\text{atom} - \text{atom}, \text{msp}^3, AO)$ (eV)	-2.26759	-0.56690	-1.13379	0	-1.13379	0
$E_T(MO)$ (eV)	-65.53833	-32.20226	-32.76916	-48.73660	-32.76916	-67.69450
ω (10^{15} rad/s)	49.7272	26.4826	11.9890	68.9812	16.2731	24.9286
E_x (eV)	32.73133	17.43132	7.89138	45.40465	10.71127	16.40846
\bar{E}_D (eV)	-0.35806	-0.26130	-0.18211	-0.42172	-0.21217	-0.25352
$\bar{E}_{K\alpha}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.15498 [54]	0.40929 [22]	0.14940 [53]	0.35532 (Eq. (13.458))
$\bar{E}_{\alpha\omega}$ (eV)	-0.25982	-0.08364	-0.10462	-0.21708	-0.13747	-0.22757
E_{mq} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(\sigma_{\text{ring}})$ (eV)	-49.54347	-32.28590	-32.87379	-49.17075	-32.90663	-67.92207
$E_{\text{initial}}(c_1, \text{aonho})$ (eV)	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489
$E_{\text{initial}}(c_1, \text{aonho})$ (eV)	0	-13.59844	0	-13.59844	0	-13.59844
$E_D(\text{group})$ (eV)	5.63881	3.90454	3.60401	7.43973	3.63685	12.49186

Table 15.247. The total bond energies of aniline and methyl-substituted anilines calculated using the functional group composition and the energies of Table 15.246 compared to the experimental values [2].

Formula	Name	C=C	C [≡] C	C [≡] H (l)	C-N (a)	NH ₂ Group	C-C (a)	C [≡] H ₂	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₆ H ₅ N	Aniline	6	0	5	1	1	0	0	64.4373	64.374	-0.00093
C ₇ H ₇ N	2-methylaniline	6	0	4	1	1	1	1	76.6245	76.643	-0.00025
C ₈ H ₉ N	3-methylaniline	6	0	4	1	1	1	1	76.6245	76.641	-0.00065
C ₉ H ₁₁ N	4-methylaniline	6	0	4	1	1	1	1	76.6245	76.654	0.00040

Table 15.248. The bond angle parameters of aniline and methyl-substituted anilines and experimental values [1]. E_r is $E_r(\text{atom} - \text{atom}, \text{mp}, \text{Å})$.

Area of Angle	2C ¹ Bond 1 (a ₁)	2C ² Bond 2 (a ₂)	2C ³ Bond 3 (a ₃)	E_r (Å)	Atom 1 Hybridization Designation (Table 15.2.4A)	E_r (Å)	Atom 2 Hybridization Designation (Table 15.2.4A)	E_r (Å)	Atom 1 C ₁	Atom 2 C ₂	C ₁	C ₂	C ₃	δ_r (eV)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle(\text{C}^1\text{C}^2\text{C}^3)$ (aromatic)	2.62036	2.62036	4.5363	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85826			120.19	120.19-32] (benzene)
$\angle(\text{C}^1\text{C}^2\text{H})$ (aromatic)															120.19		119.91	120.19-32] (benzene)
$\angle\text{HNH}$	1.88268	1.88268	3.1559	-14.53414	N	H	H	0.92613	0.92613	1	1	1	0.75	0			113.89	113.9
$\angle\text{HNH}'$	1.88268	2.60190	4.0332	-14.53414	N	-15.99555	9	0.86284	0.86284	0.75	1	1	0.75	0			122.70	(aniline)

ARYL NITRO COMPOUNDS

Aryl nitro compounds have a hydrogen of an aryl group replaced by a nitro corresponding to an NO_2 functional group and a $C-N$ functional group. Examples include nitrobenzene, nitrophenol, and nitroaniline with formulas $C_6H_5NO_2$, $C_6H_5NO_3$, and $C_6H_6N_2O_2$, respectively. The aromatic $C=C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The OH and $C-O$ functional groups of nitrophenols are the same as those of phenol given in the corresponding section. The NH_2 and $C-N$ functional groups of nitroanilines are the same as those of aniline given in the corresponding section. The differences between the total bond energies of the nitroanilines given in Table 15.252 are due to differences in the E_{arc} term. For simplicity and since the differences are small, the E_{arc} terms for nitroanilines were taken as the same.

The NO_2 group is the same as that given in the Nitroalkanes section. The bond between the nitro and aromatic ring comprises a $C-N$ functional group that is the same as that of nitroalkanes given in the corresponding section except that $E_T(atom-atom,msp^3.AO)$ is $-0.72457 eV$, one half of that of the $C-N$ -bond MO of nitroalkanes and equivalent to that of methyl (Eq. (14.151)) in order to maintain the independence and aromaticity of the benzene functional group. In addition, the energy terms due to oscillation in the transition state correspond to those of an aryl nitro compound.

The symbols of the functional groups of aryl nitro compounds are given in Table 15.249. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aryl nitro compounds are given in Tables 15.250, 15.251, and 15.252, respectively. The total energy of each aryl nitro compound given in Table 15.253 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.252 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of aryl nitro compounds determined using Eqs. (15.79-15.108) are given in Table 15.254.

Table 15.249. The symbols of functional groups of aryl nitro compounds.

Functional Group	Group Symbol
CC (aromatic bond)	C^{ar}
CH (aromatic)	CH (i)
Aryl C-N (aniline)	C-N (a)
Aryl C-N (nitro)	C-N (b)
Aryl C-O	C-O (a)
NO ₂ group	NO ₂
NH ₂ group	NH ₂
OH group	OH

Table 15.250. The geometrical bond parameters of aryl nitro compounds and experimental values [1].

Parameter	C^{ar} Group	CH (i) Group	C-N (a) Group	C-N (b) Group	C-O (a) Group	NO ₂ Group	NH ₂ Group	OH Group
a (Å)	1.47348	1.60061	1.81158	1.97794	1.68220	1.33221	1.24428	1.26430
c' (Å)	1.31468	1.03299	1.34595	1.40639	1.29700	1.15421	0.94134	0.91808
Bond Length $2c'$ (Å)	1.39140	1.09327	1.42449	1.48846	1.37268	1.22157	0.99627	0.971651
Exp. Bond Length (Å)	1.397 avg. (phenol)	1.084 (phenol)	1.431 (aniline)		1.364 (phenol)	1.224 (nitromethane)	0.998 (aniline)	0.956 (phenol)
b, c (Å)	0.66540	1.22265	1.21254	1.39079	1.07126	0.66526	0.81370	0.86925
e	0.89223	0.64537	0.74297	0.71104	0.77101	0.86639	0.75653	0.72615

Table 15.251. The MO to HOMO intercept geometrical bond parameters of α,γ nitro compounds. E_T is $E_T(\text{atom} - \text{atom}, \text{ring}, \text{AC})$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy C2sp ² (eV)	r_{bond} (Å)	$E_{\text{bond}}(\text{C2sp}^2)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (Å)	d_2 (Å)
$\text{C}^{\alpha}-\text{H}(\text{C}^{\alpha}\text{H})$	C^{α}	-0.15035	-0.15035	-0.56690	0	-151.88327	0.91771	-17.09334	74.42	105.58	39.84	1.24678	0.21279
$\text{C}_1^{\alpha}-\text{C}_2^{\alpha}-\text{H}$	(1)	-0.74804	0	0	0		1.00000	-15.37379	113.79	64.31	64.82	0.53799	0.33009
$\text{C}_1^{\alpha}-\text{C}_2^{\alpha}-\text{OH}$	C^{α}	-0.74804	-0.15035	-0.15035	0	-154.06442	0.91771	-17.27448	100.00	80.00	46.39	1.16026	0.13674
$\text{C}_1^{\alpha}-\text{C}_2^{\alpha}-\text{OH}$	(1)	-0.74804	0	0	0		1.00000	15.37379	106.51	73.49	51.43	1.04071	0.24829
$\text{C}_1^{\alpha}-\text{C}_2^{\alpha}-\text{OH}$	C^{α}	-0.74804	-0.15035	-0.15035	0	-154.06442	0.91771	-17.27448	133.88	46.12	38.55	0.70870	0.54598
$\text{C}^{\alpha}-\text{H}(\text{C}^{\alpha}\text{H})$	C^{α}	-0.15035	-0.15035	-0.56690	0	-153.88327	0.91771	-17.09334	154.26	45.76	56.98	0.75933	0.55533
$\text{C}^{\alpha}-\text{H}(\text{C}^{\alpha}\text{H})$	C^{α}	-0.15035	-0.15035	-0.56690	0	-153.88327	0.91771	-17.09334	121.74	58.26	67.49	0.47034	0.46500
$\text{C}_1^{\alpha}-\text{C}_2^{\alpha}-\text{NH}_2$	C^{α}	-0.56690	-0.15035	-0.15035	0	-153.88328	0.91771	-17.09334	81.49	91.51	41.01	1.36006	0.02101
$\text{C}_1^{\alpha}-\text{C}_2^{\alpha}-\text{NH}_2$	C^{α}	-0.56690	0	0	0		0.97084	-15.37379	96.32	81.68	46.43	1.24859	0.09796
$\text{C}_1^{\alpha}-\text{C}_2^{\alpha}-\text{H}_1$	C^{α}	-0.56690	0	0	0	-152.18259	0.91771	-15.37379	73.38	106.62	34.97	1.68027	0.35279
$\text{C}_1^{\alpha}-\text{C}_2^{\alpha}-\text{H}_1$	C^{α}	-0.56690	-0.15035	-0.15035	0	-153.88328	0.91771	-17.09334	61.56	118.44	28.27	1.14130	0.37901
$\text{RN}(\text{O})=\text{O}$	(1)	-0.97818	0	0	0		1.00000	-15.75493	133.25	44.75	66.05	0.54089	0.41333
$\text{RN}(\text{O})=\text{O}$	N	-0.97818	-0.97818	-0.36229	0	-17.04640	0.93044	-17.04640	132.36	47.64	62.44	0.61640	0.53781
$\text{C}_1^{\alpha}-\text{C}_2^{\alpha}-\text{NO}_2$	C^{α}	-0.36229	-0.15035	-0.15035	0	-153.67867	0.91771	-16.88873	72.49	107.51	33.53	1.64715	0.24256
$\text{C}_1^{\alpha}-\text{C}_2^{\alpha}-\text{NO}_2$	N	-0.92918	-0.92918	-0.36229	0		0.93044	-17.04640	71.53	108.47	32.98	1.65923	0.25294
$\text{C}_1^{\alpha}-\text{C}_2^{\alpha}-\text{NO}_2$	C^{α}	-0.36229	-0.15035	-0.15035	0	-153.67867	0.91771	-16.88873	134.63	45.35	59.47	0.74834	0.56614

Table 15.252. The energy parameters (eV) of functional groups of aryl nitro compounds.

Parameters	C=C Group	CH (i) Group	C-N (a) Group	C-N (b) Group	C-O (a) Group	NO ₂ Group	NH ₂ Group	OH Group
f_1	0.75	1						
n_1	2	1	1	1	1	2	2	1
n_2	0	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	1	0
C_1	0.5	0.75	0.5	0.5	0.5	0.5	0.75	0.75
C_2	0.85252	1	1	1	1	1	0.93613	1
c_1	1	1	1	1	1	1	0.75	0.75
c_2	0.85252	0.91771	0.84665	0.91140	0.79329	0.85987	0.92171	1
c_3	0	1	0	0	0	0	0	1
c_4	3	1	2	2	2	4	1	1
c_5	0	1	0	0	0	0	2	1
C_{10}	0.5	0.75	0.5	0.5	0.5	0.5	1.5	0.75
C_{20}	0.85252	1	1	1	1	1	1	1
V_p (eV)	-101.12679	-37.10024	-32.76465	-31.36351	-34.04658	-106.90919	-78.97795	-40.92709
V_p (eV)	20.69825	13.17125	10.10870	9.67426	10.49024	23.57588	28.90735	14.81988
T (eV)	34.31559	11.58941	9.04312	7.92833	10.11966	40.12475	31.73641	16.18567
V_m (eV)	-17.15779	-5.79470	-4.52156	-3.96416	-5.05983	-20.06238	-15.86820	-8.09284
$\Delta E(\text{atom})$ (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	0	-14.53414	-13.6181
$\Delta E_{H,100}(\text{atom})$ (eV)	0	-1.13379	-1.13379	-0.72457	-1.49608	0	0	0
$E_p(\text{atom})$ (eV)	0	-13.50110	-13.50110	-13.91032	-13.13881	0	-14.53414	-13.6181
$E_{10}(\text{atom})$ (eV)	0	0	0	0	0	0	-14.53414	0
$E_{10}(\text{atom})$ (eV)	-63.27075	-31.63539	-31.63549	-31.63540	-31.63532	-63.27093	-48.73654	-31.63247
$E_{10}(\text{atom} - \text{atom}_{msp}, AO)$ (eV)	-2.26759	-0.56690	-1.13379	-0.72457	-1.49608	-3.71673	0	0
$E_{10}(\text{atom})$ (eV)	-65.53833	-32.20226	-32.76916	-32.35994	-33.13145	-66.98746	-48.73660	-31.63537
ω (10^{15} rad/s)	49.7272	26.4826	11.9890	17.8228	13.3984	19.0113	68.9812	44.1776
E_K (eV)	32.73133	17.43132	7.89138	11.73128	8.81907	12.51354	45.40465	29.07844
\bar{E}_D (eV)	-0.35806	-0.26130	-0.18211	-0.21927	-0.19465	-0.23440	-0.42172	-0.33749
\bar{E}_{K10} (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.15498 [54]	0.10539 [45]	0.12808 [19]	0.19342 [45]	0.40929 [22]	0.46311 [17-18]
\bar{E}_{cur} (eV)	-0.25982	-0.08364	-0.10462	-0.16658	-0.13061	-0.13769	-0.21708	-0.10594
E_{aug} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.11441	0.14803	0.11441
$E_{10}(\text{atom})$ (eV)	-49.54347	-32.28590	-32.87379	-32.52652	-33.26206	-67.26284	-49.17075	-31.74130
$E_{1000}(\text{atom})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414	-13.6181
$E_{1000}(\text{atom})$ (eV)	0	-13.59844	0	0	0	0	-13.59844	-13.59844
$E_D(\text{atom})$ (eV)	5.63881	3.90454	3.60401	3.25674	3.99228	8.72329	7.43973	4.41035

Table 15.253. The total bond energies of aryl nitro compounds calculated using the functional group composition and the energies of Table 15.252 compared to the experimental values [2]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the E_g (see) (e) values based on composition is given by (15.58).

Formula	Name	$C=C$	CH (i)	$C-N$ (a)	$C-N$ (b)	$C-O$ (a)	NO_2	NH_2	OH	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_6H_5NO_2$	Nitrobenzene	6	3	0	1	0	1	0	0	1	65.1754	65.277	0.00046
$C_6H_4(NO_2)_2$	2,4-dinitrophenol	6	4	0	2	1	2	0	1	2	77.6108	77.642	0.00007
$C_6H_4(NO_2)_2$	2-nitrophenol	6	4	1	1	0	1	0	0	0	72.47476	72.474	-0.00070
$C_6H_4(NO_2)_2$	2-nitrophenol	6	4	1	1	0	1	1	0	0	72.47476	72.481	-0.00009
$C_6H_4(NO_2)_2$	4-nitrophenol	6	4	1	1	0	1	1	0	0	72.47476	72.476	-0.00002

Table 15.254. The bond angle parameters of aryl nitro compounds and experimental values [1]. E_r is $E_r(atom - atom, mp, AO)$.

Atom or Angle	ZC' Bond 1 (σ_1)	ZC' Bond 2 (σ_2)	ZC' Terminal Atom (σ_3)	$E_{r,calc}$ Atom 1	$E_{r,calc}$ Atom 2	$E_{r,calc}$ Atom 3	Hybridization Designation	σ_1 Atom 1	σ_2 Atom 2	σ_3 Atom 3	C_1	C_2	η	ζ	E_r (eV)	θ_r ($^\circ$)	θ_s ($^\circ$)	Calc. θ ($^\circ$)	Exp. θ ($^\circ$)
$ZCCC'$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	-17.17218	-17.17218	34	0.79232	0.79232	0.79232	1	1	1	0.79232	-1.83136			120.19	120.19 (benzene)
$ZCCH$ (aromatic)	2.30843	2.30843	4.1231	-16.68411	-16.68411	-16.68411	24	0.81549	0.81549	0.81549	1	1	1	0.81549	-1.44915			126.52	126.52 (nitrobenzene)
$ZCNO$	2.81279	2.30843	4.4159	-17.45362	-13.61806	-13.61806	0	0.77943	0.77943	0.85953 (Eq. (15.114))	1	1	1	0.81670	-1.63776			118.82	118.5 (4) (nitrobenzene)
$ZC'OH$	2.39399	1.83616	3.6515	-14.82375	-14.82375	-14.82375	1	1	0.91771	0.91771	0.75	1	0.75	0.91771	0			109.84	109.8 (phenol)
$ZINH$	1.8268	1.8268	3.1539	-14.53414	-14.53414	-14.53414	H	0.84665 (Eq. (15.124))	0.84665	0.84665	1	1	1	1.06823	0			113.89	113.9 (aniline)
$ZC'NH$	2.69190	1.88268	3.9833	-15.99585	-15.99585	-15.99585	9	0.84665 (Eq. (15.122))	0.84665	0.84665	0.75	1	0.75	1.00100	0			120.05	

BENZOIC ACID COMPOUNDS

Benzoic acid compounds have a hydrogen of an aryl group replaced by a carboxylic acid group corresponding to an $C-C(O)-OH$ moiety that comprises $C=O$ and OH functional groups that are the same as those of carboxylic acids given in the corresponding 5 section. The single bond of aryl carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. This group is also equivalent to the same group of carboxylic acids except that $\Delta E_{H_1MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom-atom,msp^3.AO)$ in Eq. (15.52) are both -1.29147 eV which is a linear combination of $\frac{-1.13379\text{ eV}}{2}$, $E_T(atom-atom,msp^3.AO)$ of the $C-H$ group that the $C-C(O)$ group replaces, and that 10 of an independent $C2sp^3\text{ HO}$, -0.72457 eV (Eq. (14.151)).

Examples include benzoic acid, chlorobenzoic acid, and aniline carboxylic acid with formulas $C_7H_6O_2$, $C_7H_5O_2Cl$, and $C_7H_7NO_2$, respectively. The aromatic $C=C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic 15 Compounds section. The NH_2 and $C-N$ functional groups of aniline carboxylic acids are the same as those of aniline given in the corresponding section. The $C-Cl$ functional group of 2-chlorobenzoic acids corresponding to meta substitution is equivalent to that of chlorobenzene given in the corresponding section. The $C-Cl$ functional group of 3 or 4-chlorobenzoic acids corresponding to ortho and para substitution is also equivalent to that of 20 chlorobenzene, except that $\Delta E_{H_1MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom-atom,msp^3.AO)$ in Eq. (15.52) are both -0.92918 eV (Eq. (14.513)) since each of these positions can form a resonance structure with the carboxylic acid group which is permissive of greater charge donation from the $C2sp^3\text{ HO}$.

The symbols of the functional groups of benzoic acid compounds are given in Table 25 15.255. The corresponding designations of benzoic acid is shown in Figure 64. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of benzoic acid compounds are given in Tables 15.256, 15.257, and 15.258, respectively. The total energy of each benzoic acid compound given in Table 15.259 was calculated as the sum over the integer multiple of

each $E_D(\text{Group})$ of Table 15.258 corresponding to functional-group composition of the molecule. The bond angle parameters of benzoic acid compounds determined using Eqs. (15.79-15.108) are given in Table 15.260.

5 Table 15.255. The symbols of functional groups of benzoic acid compounds.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{3e}{C=C}$
CH (aromatic)	CH (i)
C-C(O)	C-C(O)
C=O (aryl carboxylic acid)	C=O
(O)C-O	C-O
OH group	OH
Cl-C (Cl to aromatic bond of 2-chlorobenzoic acid)	C-Cl (i)
Cl-C (Cl to aromatic bond of 3 or 4-chlorobenzoic acid)	C-Cl (ii)
Aryl C-N (aniline)	C-N
NH ₂ group	NH ₂

Table 15.256. The geometrical bond parameters of benzoic acid compounds and experimental values [1].

Parameter	C=C Group	CH (i) Group	C-C(O) Group	C=O Group	C-O Group	C=O Group	OH Group	C-Cl (i) Group	C-Cl (ii) Group	C-N Group	NH ₂ Group
a (Å)	1.47348	1.60061	1.95111	1.29907	1.73490	1.26430	1.26430	2.20759	2.19358	1.81158	1.24428
c' (Å)	1.31468	1.03299	1.39682	1.13977	1.31716	0.91808	0.91808	1.64782	1.64743	1.34595	0.94134
Bond Length	1.39140	1.09327	1.47833	1.20628	1.39402	0.971651	0.971651	1.74397	1.73827	1.42449	0.99627
Exp. Bond Length (Å)	1.399 (benzene)	1.101 (benzene)	1.48 [55] (benzoic acid)	1.214 (acetic acid)	1.393 (methyl formate)	0.972 (formic acid)	0.972 (formic acid)	1.737 (chlorobenzene)	1.737 (chlorobenzene)	1.431 (aniline)	0.998 (aniline)
$A_{s,c}$ (Å)	0.66340	1.22265	1.36223	0.62331	1.12915	0.86925	0.86925	1.46967	1.45403	1.21234	0.81370
ϵ	0.89223	0.64537	0.71391	0.87737	0.75921	0.72613	0.72613	0.74630	0.74874	0.74297	0.75633

Table 15.258. The energy parameters (eV) of functional groups of benzoic acid compounds.

Table 15.256. The energy parameters (eV) of functional groups of benzoic acid compounds.

Parameters	C=C Group	ν Group	(ν (f) Group	C=O Group	C=O Group	C=O Group	C=O Group	ν Group	ν Group	C-N Group	NH ₂ Group
J_1	0.75	1	1	1	2	1	1	1	1	1	2
η_1	2	0	0	0	0	0	0	0	0	0	0
η_2	0	0	0	0	0	0	0	0	0	0	1
η_3	0.5	0.75	0.5	0.5	0.5	0.75	0.75	0.5	0.5	0.5	0.75
ζ_1	0.85252	1	1	1	1	1	0.81317	0.81317	1	0.95613	0.95613
ζ_2	1	1	1	1	1	0.75	1	1	1	0.75	0.75
ζ_3	0.85252	0.91771	0.91771	0.85295	0.85295	1	1	1	0.84665	0.92171	0.92171
ζ_4	0	1	0	2	0	1	0	0	0	0	0
ζ_5	3	1	2	4	2	1	2	2	2	2	1
ζ_6	0	1	0	0	0	0	0	0	0	0	2
ζ_7	0.5	0.75	0.5	0.5	0.5	0.75	0.5	0.5	0.5	0.5	1.5
ζ_8	0.85252	1	1	1	1	1	0.81317	0.81317	1	1	1
ζ_9	-101.12679	-37.10024	-32.15216	-111.24473	-35.08488	-40.92709	-31.85648	-32.14474	-32.76465	-78.97795	-78.97795
ν_1 (eV)	20.69823	13.7123	9.74055	23.87467	10.32968	14.81988	8.26586	8.26586	10.10870	23.80735	23.80735
ν_2 (eV)	34.31559	11.58841	8.23945	42.82081	10.11150	16.18567	7.21391	7.21391	9.04312	31.73641	31.73641
ν_3 (eV)	-17.15779	-5.79470	-4.11973	-21.41040	-0.50575	-8.09284	-3.60695	-3.60695	-4.52156	-15.86820	-15.86820
ΔE_{HOMO} (eV)	0	-14.63489	-14.63489	0	-14.63489	-13.6181	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
ΔE_{HOMO} (eV)	0	-1.13379	-1.20147	-2.69895	-2.69895	-11.93596	-2.69895	-2.69895	-2.69895	-1.13379	0
F_1 (eV)	0	-13.50110	-13.34342	2.69893	-11.93596	-13.6181	-11.64273	-11.64273	-13.50110	-14.53414	-14.53414
F_2 (eV)	0	0	0	0	0	0	0	0	0	-14.53414	-14.53414
F_3 (eV)	-63.27075	-31.63539	-31.63530	-63.27074	-31.63541	-31.63247	-31.63539	-31.63542	-31.63549	-48.73654	-48.73654
E_T (eV)	-2.26759	-0.56690	-1.29147	-2.69895	-1.85136	0	-0.72457	-0.92918	-1.13379	0	0
E_T (eV)	-65.53833	-32.20226	-32.92684	-65.90965	-33.49237	-31.63537	-32.35994	-32.56455	-32.76916	-48.73660	-48.73660
ω (10 ¹⁵ rad/s)	49.7272	26.4826	10.7262	59.4034	24.3637	44.1776	8.03459	8.11389	11.9890	68.9812	68.9812
E_1 (eV)	32.73133	17.43132	7.06019	39.10034	16.03560	29.07844	5.28851	5.34070	7.89138	45.40465	45.40465
E_2 (eV)	-0.38606	-0.26130	-0.17909	-0.40804	-0.26535	-0.33749	-0.47722	-0.14888	-0.18211	-0.42172	-0.42172
E_3 (eV)	0.19649	0.35532	0.10502	0.21077	0.14010	0.64511	0.08059	0.15098	0.40929	0.40929	0.40929
E_4 (eV)	[69]	E_4 (13.458)	[29]	[12]	[31]	[17-18]	[12]	[54]	[23]	[23]	[23]
E_5 (eV)	-0.25982	-0.08564	-0.12038	-0.30266	-0.19530	-0.10594	-0.10693	-0.10819	-0.10462	-0.21708	-0.21708
E_6 (eV)	0.14803	0.14803	0.11441	0.14803	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803
E_7 (eV)	-49.54347	-32.78590	-33.04742	-66.57498	-33.68903	-31.74130	-32.16687	-32.67314	-32.87379	-49.17075	-49.17075
E_{HOMO} (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-13.6181	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
E_{HOMO} (eV)	0	-13.50444	0	0	0	-13.59844	0	0	0	0	-13.59844
E_{HOMO} (eV)	3.90634	3.77764	7.80660	4.41925	4.41925	3.19709	3.40336	3.40336	3.60401	7.43973	7.43973

ANISOLE

Anisole has the formula C_7H_8O and comprises the phenol molecule with the hydroxyl hydrogen atom replaced by the moiety $-O-CH_3$ to form an ether comprising aromatic and methyl functional groups as well as two types of $C-O$ functional groups, one for aryl carbon to oxygen and one for methyl carbon to oxygen. The aromatic $C=C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The CH_3 and methyl $C-O$ functional groups are the same as those of the corresponding ether groups given in the corresponding section.

The $C-O$ functional group comprising the bond between the ether oxygen and aromatic ring is equivalent to that of the methyl ether $C-O$ functional group except that $\Delta E_{H,MO}(AO/HO)$ in Eq. (15.42) and $E_r(atom-atom,msp^3.AO)$ in Eq. (15.52) are both -1.13379 eV (Eq. (14.247)). $E_r(atom-atom,msp^3.AO)$ is based on the energy match between the OCH_3 group and the $C2sp^3$ HO of the aryl group and is twice that of the aryl $C-H$ group that it replaces.

The symbols of the functional groups of anisole are given in Table 15.261. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of anisole are given in Tables 15.262, 15.263, and 15.264, respectively. The total energy of anisole given in Table 15.265 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.264 corresponding to functional-group composition of the molecule. The bond angle parameters of anisole determined using Eqs. (15.79-15.108) are given in Table 15.266.

Table 15.261. The symbols of functional groups of anisole.

Functional Group	Group Symbol
CC (aromatic bond)	$C=C$
CH (aromatic)	CH (i)
Aryl C-O	$C-O$ (a)
Methyl C-O	$C-O$ (b)
CH_3 group	$C-H$ (CH_3)

Table 15.262. The geometrical bond parameters of anisole and experimental values [1].

Parameter	C=C Group	C-H (i) Group	C-O (i) Group	C-H (CH ₃) Group
σ (Å)	1.47248	1.60051	1.82682	1.80717
σ' (Å)	1.31468	1.03299	1.35160	1.34431
Bond Length	1.39140	1.09327	1.43047	1.10974
Exp. Bond Length (phenol) (Å)	1.397 avg.	1.084		1.111 (avg.)
b.c (Å)	0.65340	1.22765	1.20776	1.27295
ϵ	0.89223	0.64537	0.73986	0.63580

Table 15.263. The MO to HO intercept geometrical bond parameters of anisole. E_r is $E_r(\text{atom} - \text{atom}, \text{exp}, \text{AO})$.

Bond	Atom	E_r (eV) Bond 1	E_r (eV) Bond 2	E_r (eV) Bond 3	E_r (eV) Bond 4	Final Total Energy C_{2sp^2} (eV)	r_{new} (Å)	r_{exp} (Å)	$E_{\text{atom}}(C_{2sp^2})$ (eV) Final	$E(C_{2sp^2})$ (eV) Final	θ' (°)	θ (°)	θ_2 (°)	d_1 (Å)	d_2 (Å)
C-H (C ₁ H)	C ₁	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09324	-16.90248	74.42	105.53	33.84	1.26678	0.21379
C-H (OC ₂ H ₃)	C ₂	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.53033	-15.33546	78.85	101.15	42.40	1.21777	0.16921
(C ₂ ^{sp}) C ₂ O-C ₂ H ₃	C ₂	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.53033	-15.33546	95.98	84.02	46.10	1.23319	0.09112
(C ₂ ^{sp}) C ₂ O-C ₂ H ₃	O	-0.72457	-0.56690	0	0		1.00000	0.84418	-16.11722		93.38	84.62	44.35	1.29456	0.04975
(C ₂ ^{sp}) C ₂ -OC ₂ H ₃	C ₂	-0.56690	-0.85035	-0.85035	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	87.00	93.00	40.10	1.38329	0.04170
(C ₂ ^{sp}) C ₂ -OC ₂ H ₃	O	-0.56690	-0.72457	0	0		1.00000	0.84418	-16.11722		91.59	84.41	43.36	1.32814	0.02346
(C ₂ ^{sp}) C ₂ OC ₂ H ₃	C ₂	-0.56690	-0.85035	-0.85035	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.73935	0.55333
(C ₂ ^{sp}) C ₂ OC ₂ H ₃	C ₂	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.73935	0.55333

Table 15.264. The energy parameters (eV) of functional groups of anisole.

Parameters	C=C Group	CH (f) Group	C-O (a) Group	C-O (b) Group	CH ₃ Group
f_1	0.75	1			
n_1	2	1	1	1	3
n_2	0	0	0	0	2
n_3	0	0	0	0	0
C_1	0.5	0.75	0.5	0.5	0.75
C_2	0.85252	1	1	1	1
C_3	0.85252	0.91771	0.85395	0.85395	0.91771
C_4	0	1	0	0	0
C_5	3	1	2	2	1
C_6	0	1	0	0	3
C_{10}	0.5	0.75	0.5	0.5	0.75
C_{10}^*	0.85252	1	1	1	1
V_1 (eV)	-101.12679	-37.10024	-32.67197	-33.15757	-107.32728
V_2 (eV)	20.69825	13.17125	10.06645	10.12103	38.92728
T (eV)	34.31559	11.58941	8.94231	9.17389	32.53914
V_3 (eV)	-17.15779	-5.79470	-4.47115	-4.38695	-16.26957
$E_{(aniso)}$ (eV)	0	-14.63489	-14.63489	-14.63489	-15.56407
$\Delta E_{H_{2O}}$ (eV)	0	-1.13379	-1.13379	-1.44915	0
E_T (eV)	0	-13.50110	-13.50110	-13.18574	-15.56407
E_T (eV)	-63.27075	-31.63539	-31.63547	-31.63533	-67.69451
E_T (atom - atom, msp, AO) (eV)	-2.26759	-0.56690	-1.13379	-1.44915	0
E_T (eV)	-65.53833	-32.20226	-32.76916	-33.08452	-67.69450
ω (10^3 rad/s)	49.7272	26.4826	11.8393	12.0329	24.9286
E_C (eV)	32.73133	17.43132	7.79284	7.92028	16.40846
E_D (eV)	-0.35806	-0.26130	-0.18097	-0.18420	-0.25352
$E_{K\alpha}$ (eV)	0.19649	0.35532	0.13663	0.13663	0.35532
$E_{K\alpha}$ (eV)	[49]	Eq. (13.458)	[21]	[21]	(Eq. (13.458))
$E_{K\alpha}$ (eV)	-0.25982	-0.08364	-0.11266	-0.11589	-0.22757
$E_{K\alpha}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803
E_T (eV)	-49.54347	-32.28590	-32.88182	-33.20040	-67.92207
$E_{K\alpha}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{K\alpha}$ (eV)	0	-13.59844	0	0	-13.59844
E_D (eV)	5.63881	3.90454	3.61204	3.93062	12.49186

Table 15.265. The total bond energies of anisole calculated using the functional group composition and the energies of Table 15.264 compared to the experimental values [2].

Formula	Name	$C^N=C$	$C^H(I)$	Group	$C-U(b)$	Group	CH_2	Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_6H_5O	Anisole	6	3	1	1	1	1	1	73.39006	73.335	-0.00047

Table 15.266. The bond angle parameters of anisole and experimental values [1]. E_r is $E_r(\text{atom} - \text{atom}, \text{exp}, \text{AO})$.

Atoms of Angle	$2C^*$ Bond 1 (a_1)	$2C^*$ Bond 2 (a_2)	$2C^*$ Terminal Atom (a_3)	E_{terminal} Atom 1	Hybridization Designation (Table 15.3.A)	E_{terminal} Atom 2	Hybridization Designation (Table 15.3.A)	E_3 Atom 1	E_3 Atom 2	C_1	C_2	C_3	ζ_1	ζ_2	E_r (eV)	θ_1 ($^\circ$)	θ_2 ($^\circ$)	θ_3 ($^\circ$)	Cal. θ ($^\circ$)	Exp. θ ($^\circ$)
$\angle C-C-C$ (anisole)	2.62936	2.62936	4.5385	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	1	0.79232	-1.85836				120.19	120 [15b-32] (benzene)
$\angle C-C-H$ (anisole)																			120.19	120 [15b-32] (benzene)

PYRROLE

Pyrrole having the formula C_4H_5N comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to a NH functional group. The two symmetrical carbon-to-nitrogen bonds comprise the $C-N-C$ functional group. The 1,3-
 5 butdiene moiety comprises $C-C$, $C=C$, and CH functional groups. The $C-C$ and $C=C$ groups are equivalent to the corresponding groups of 1,3-butdiene given in the Cyclic and Conjugated Alkenes section except that the energies terms of the corresponding to oscillation in the transition state match pyrrole. Furthermore, the conjugated double bonds have the same bonding as in 1,3-butdiene except that the hybridization terms c_2 of the $C-C$
 10 and $C=C$ groups and C_2 and C_{2o} of the $C=C$ group in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143), $(C_2(benzeneC2sp^3HO) = c_2(benzeneC2sp^3HO) = 0.85252)$, in the cyclic pyrrole MO which has aromatic character. The bonding in pyrrole, furan, and thiophene are the same except for the energy match to the corresponding heteroatoms. The hybridization permits double-bond
 15 character in the carbon-heteroatom bonding.

The NH group is solved equivalently to that of a secondary amine as given in the corresponding section except that the hybridization term c_2 is that of the amino group of aniline in order provide double-bond character to match the group to the other orbitals of the molecule. Similarly, the CH functional group is equivalent to that of 1,3-butdiene, except
 20 that $\Delta E_{H_1MO}(AO/HO) = -2.26758 \text{ eV}$ (Eq. (14.247)) in Eq. (15.42) in order to provide matching double-bond character.

The solution of the $C-N-C$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs and the nitrogen atom to form a MO permits
 25 each participating hybridized orbital to decrease in radius and energy. Thus, the $C-N-C$ -bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1 = 2$ in Eqs. (15.42) and (15.52). The hybridization factor $c_2(arylC2sp^3HO \text{ to } N) = 0.84665$ (Eq. (15.152)) matches the double-bond character of the $C2sp^3$ HOs to the N atom of the NH group, and C_2 and C_{2o} in Eqs. (15.42) and (15.52).

become that of benzene given by Eq. (15.143), $C_2(\text{benzene}C2sp^3HO) = 0.85252$. Furthermore, $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.42) and $E_T(\text{atom-atom}, msp^3.AO)$ in Eq. (15.52) are both -0.92918 eV (Eq. (14.513)) per atom corresponding to -3.71673 eV in total. This is the maximum energy for a single bond and corresponds to methylene character 5 as given in the Continuous-Chain Alkanes section.

The symbols of the functional groups of pyrrole are given in Table 15.267. The structure of pyrrole is shown in Figure 65. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of pyrrole are given in Tables 15.268, 15.269, and 15.270, respectively. The total energy of 10 pyrrole given in Table 15.271 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.270 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrrole determined using Eqs. (15.79-15.108) are given in Table 15.272.

15 Table 15.267. The symbols of functional groups of pyrrole.

Functional Group	Group Symbol
$C_a = C_b$ double bond	$C = C$
$C_b - C_b$	$C - C$
$C_a - N - C_a$	$C - N - C$
NH group	NH
CH	CH

Table 15.268. The geometrical bond parameters of pyrrole and experimental values [1].

Parameter	C = C Group	C - C Group	C - N - C Group	NH Group	CH Group
a (a_0)	1.45103	1.77965	1.43222	1.24428	1.53380
c' (a_0)	1.30463	1.33404	1.29614	0.94134	1.01120
Bond Length $2c'$ (\AA)	1.38076	1.41188	1.37178	0.996270	1.07021
Exp. Bond Length (\AA)	1.382 (pyrrole)	1.417 (pyrrole)	1.370 (pyrrole)	0.996 (pyrrole)	1.076 (pyrrole)
b, c (a_0)	0.63517	1.17792	0.60931	0.81370	1.15326
e	0.89910	0.74961	0.90499	0.75653	0.65928

Table 15.269. The MO to HO intercept geometrical bond parameters of pyrrole. R is an alkyl group and R', R'', R''' are H or alkyl groups. E_r is $E_r(\text{atom} - \text{atom}, \text{mip}, \text{AO})$.

Bond	Atom	E_r (eV) Bond 1	E_r (eV) Bond 2	E_r (eV) Bond 3	E_r (eV) Bond 4	Final Total Energy (2sp ²) (eV)	r_{mip} (a ₀)	E_{mip} (eV) Final	$E(\text{2sp}^2)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a ₀)	d_2 (a ₀)
$C'-H(C', H)$	C'	-1.13380	-0.92518	0	0	-153.67867	0.91771	-16.88872	-16.69786	83.23	96.65	43.94	1.10432	0.09331
$C'-H(C', H)$	C'	-1.13380	-1.13380	0	0	-153.83328	0.91771	-17.09334	-16.90248	82.21	97.79	43.14	1.11914	0.10794
$C_2 = (H)C_3 - C_4(H) = C_5$	C ₄	-1.13380	-1.13380	0	0	-153.83328	0.91771	-17.09334	-16.90248	91.57	88.43	42.49	1.31226	0.03177
$C_2 = C_4(H)C_3 = C_5$	C ₃	-1.13380	-1.13380	0	0	-153.83328	0.91771	-17.09334	-16.90248	136.36	43.64	59.86	0.72857	0.57606
$HNC_2 = C_4(H)$	C ₄	-1.13380	-0.92518	0	0	-153.67867	0.91771	-16.88872	-16.69786	136.73	43.23	60.35	0.71764	0.38678
$C_4(H)N - C_2 = C_3(H)$	C ₂	-1.13380	-0.92518	0	0	-153.67867	0.91771	-16.88872	-16.69786	138.54	41.46	61.09	0.69238	0.60376
$C_4(H)N - C_2 = C_3(H)$	N	-0.92518	-0.92518	0	0		0.92084	-16.88411		138.92	41.08	61.59	0.61447	0.61467
$N-H(NH)$	N	-0.92518	-0.92518	0	0		0.92084	-16.88411		117.34	62.66	62.90	0.36678	0.37456

Table 15.270. The energy parameters (eV) of functional groups of pyrrole.

Parameters	C=C Group	C-C Group	C-N-C Group	NH Group	CH Group
n_1	2	1	2	1	1
n_2	0	0	0	0	0
n_3	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75
C_2	0.85252	1	0.85252	0.93613	1
c_1	1	1	1	0.75	1
c_2	0.85252	0.85252	0.84665	0.92171	0.91771
c_3	0	0	0	1	1
c_4	4	2	4	1	1
c_5	0	0	0	1	1
C_{10}	0.5	0.5	0.5	0.75	0.75
C_{20}	0.85252	1	0.85252	1	1
V_e (eV)	-104.37986	-33.80733	-106.58684	-39.48897	-39.09538
V_p (eV)	20.85777	10.19898	20.99432	14.45367	13.45505
T (eV)	35.96751	9.49831	37.21047	15.86820	12.74462
V_n (eV)	-17.98376	-4.74915	-18.60523	-7.93410	-6.37231
$E(\text{AO} \text{HO})$ (eV)	0	-14.63489	0	-14.53414	-14.63489
$\Delta E_{H,MO}(\text{AO} \text{HO})$ (eV)	-2.26759	-1.85836	-3.71673	0	-2.26758
$E_T(\text{AO} \text{HO})$ (eV)	2.26759	-12.77653	3.71673	-14.53414	-12.36731
$E_T(H,MO)$ (eV)	-63.27075	-31.63572	-63.27056	-31.63534	-31.63533
$E_T(\text{atom} - \text{atom}, msp^3, \text{AO})$ (eV)	-2.26759	-2.26759	-3.71673	0	0
$E_T(MO)$ (eV)	-65.53833	-33.90295	-66.98746	-31.63537	-31.63537
ω (10^{15} rad/s)	15.4421	12.3131	15.7474	48.7771	28.9084
E_K (eV)	10.16428	8.10471	10.36521	32.10594	19.02803
\bar{E}_D (eV)	-0.20668	-0.19095	-0.21333	-0.35462	-0.27301
$\bar{E}_{K\text{Hb}}$ (eV)	0.17897 [6]	0.14829 [48]	0.11159 [12]	0.40696 [24]	0.39427 [56]
\bar{E}_{osc} (eV)	-0.11720	-0.11680	-0.15754	-0.15115	-0.07587
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(\text{group})$ (eV)	-65.77272	-34.01976	-67.30254	-31.78651	-31.71124
$E_{inlet}(c_1, \text{AO} \text{HO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489
$E_{inlet}(c_3, \text{AO} \text{HO})$ (eV)	0	0	0	-13.59844	-13.59844
$E_D(\text{group})$ (eV)	7.23317	4.74998	8.76298	3.51208	3.32988

FURAN

Furan having the formula C_4H_4O comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to an oxygen atom. The two symmetrical carbon-to-oxygen bonds comprise the $C-O-C$ functional group. The 1,3-butdiene moiety comprises $C-C$, $C=C$, and CH functional groups. The CH , $C-C$, and $C=C$ groups are equivalent to the corresponding groups of pyrrole given in the corresponding section.

The $C-O-C$ functional group of furan is solved in a similar manner as that of the $C-N-C$ group of pyrrole. The solution of the $C-O-C$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs and the oxygen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the $C-O-C$ -bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n = 2$ in Eqs. (15.42) and (15.52). The hybridization factor $c_2(arylC2sp^3HO \text{ to } O) = 0.79329$ (Eq. (15.150)) matches the double-bond character of the $C2sp^3$ HOs to the O atom, and C_2 and C_{2o} in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143), $C_2(benzeneC2sp^3HO) = 0.85252$. Furthermore, $E_T(atom - atom, msp^3.AO)$ in Eq. (15.52) is -0.92918 eV (Eq. (14.513)) per atom corresponding to -3.71673 eV in total.

The symbols of the functional groups of furan are given in Table 15.273. The structure of furan is shown in Figure 66. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of furan are given in Tables 15.274, 15.275, and 15.276, respectively. The total energy of furan given in Table 15.277 was calculated as the sum over the integer multiple of each $E_D(group)$ of Table 15.276 corresponding to functional-group composition of the molecule. The bond angle parameters of furan determined using Eqs. (15.79-15.108) are given in Table 15.278.

Table 15.273. The symbols of functional groups of furan.

Functional Group	Group Symbol
$C_n = C_n$ double bond	$C = C$
$C_n - C_n$	$C - C$
$C_n - O - C_n$	$C - O - C$
CH	CH

Table 15.274. The geometrical bond parameters of furan and experimental values [1].

Parameter	$C = C$ Group	$C - C$ Group	$C - O - C$ Group	CH Group
σ (a_0)	1.45103	1.77965	1.41546	1.33380
σ' (a_0)	1.30463	1.33404	1.28854	1.01120
Bond Length $2a'$ (Å)	1.38076	1.41188	1.36373	1.07021
Exp. Bond Length (Å)	1.361 (furan)	1.431 (furan)	1.362 (furan)	1.075 (furan)
$h.c.$ (a_0)	0.63317	1.17792	0.58583	1.15226
ϵ	0.89910	0.74961	0.91053	0.65928

Table 15.275. The MO to HO intercept geometrical bond parameters of furan. R_i is an alkyl group and R, R', R'' are H or alkyl groups. E_T is $E_T(\text{atom} - \text{atom}, \text{map}, \text{AO})$.

Bond	Atom	R_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy C_{2sp^2} (eV)	r_{bond} (a_0)	r_{bond} (a_0)	$E_{\text{bond}}(C_{2sp^2})$ (eV) Final	$E(C_{2sp^2})$ (eV) Final	θ' (°)	θ_i (°)	θ_j (°)	d_i (a_0)	d_j (a_0)
$C-H$ (C, H)	C_1	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	83.35	96.65	43.94	1.10452	0.09331
$C-H$ (C, H)	C_2	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79997	-17.09334	-16.90248	82.21	97.79	43.14	1.11914	0.10794
$C_n = (H)C_n - (C_n)(H) = C_n$	C_3	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79997	-17.09334	-16.90248	91.57	88.43	42.49	1.31226	0.02177
$C_n = C_n(C_n)(H)(C_n) = C_n$	C_4	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79997	-17.09334	-16.90248	136.36	43.64	59.86	0.72857	0.57606
$(H)C_n = C_n(C_n)(H)$	C_5	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	136.75	43.25	60.35	0.71784	0.58678
$C_n O - C_n = C_n(H)$	C_6	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	140.16	39.84	61.75	0.66992	0.61862
$C_n O - C_n = C_n(H)$	C_7	-0.92918	-0.92918	0	0	-153.67867	1.00000	0.81549	-16.68411	-16.69786	140.52	39.48	62.25	0.65906	0.62947

Table 15.276. The energy parameters (eV) of functional groups of furan.

Parameters	C = C Group	C - C Group	C - O - C Group	CH Group
n_1	2	1	2	1
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.5	0.5	0.75
C_2	0.85252	1	0.85252	1
c_1	1	1	1	1
c_2	0.85252	0.85252	0.79329	0.91771
c_3	0	0	0	1
c_4	4	2	4	1
c_5	0	0	0	1
C_{1o}	0.5	0.5	0.5	0.75
C_{2o}	0.85252	1	0.85252	1
V_e (eV)	-104.37986	-33.80733	-102.49036	-39.09538
V_p (eV)	20.85777	10.19898	21.11822	13.45505
T (eV)	35.96751	9.49831	36.20391	12.74462
V_m (eV)	-17.98376	-4.74915	-18.10196	-6.37231
$E(\text{AOIHO})$ (eV)	0	-14.63489	0	-14.63489
$\Delta E_{H_2MO}(\text{AOIHO})$ (eV)	-2.26759	-1.85836	0	-2.26758
$E_T(\text{AOIHO})$ (eV)	2.26759	-12.77653	0	-12.36731
$E_T(H_2MO)$ (eV)	-63.27075	-31.63572	-63.27019	-31.63533
$E_T(\text{atom-atom,msp}^3.AO)$ (eV)	-2.26759	-2.26759	-3.71673	0
$E_T(MO)$ (eV)	-65.53833	-33.90295	-66.98746	-31.63537
ω (10^{15} rad/s)	15.4421	12.3131	58.0664	28.9084
E_K (eV)	10.16428	8.10471	38.22034	19.02803
\bar{E}_D (eV)	-0.20668	-0.19095	-0.40965	-0.27301
\bar{E}_{Kvib} (eV)	0.17897 [6]	0.14829 [48]	0.12523 [57]	0.39427 [56]
\bar{E}_{usc} (eV)	-0.11720	-0.11680	-0.34704	-0.07587
E_{mog} (eV)	0.14803	0.14803	0.14803	0.14803
$E_T(cirrup)$ (eV)	-65.77272	-34.01976	-67.68154	-31.71124
$E_{initial}(c_1 \text{ AOIHO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5 \text{ AOIHO})$ (eV)	0	0	0	-13.59844
$E_D(cirrup)$ (eV)	7.23317	4.74998	9.14198	3.32988

C ₁ H ₄	Calculated		Experimental	Total Bond Energy (eV)	Relative Error
	2	4			
CH ₄ O	41.57782	41.57782	41.592	0.00033	

Table 13.278. The bond angle parameters of furan and experimental values [1]. In the calculation of θ_r , the parameters from the preceding angle were used. E_r is $E_r(\text{atom} - \text{atom}, \text{map}^2 \cdot \text{AO})$.

Atom or Angle	2c' (a ₁)	2c' Bond 2 (a ₁)	2c' Terminal Atom (a ₁)	E _{Covalent} Atom 1 Hybridization Designation (Table 15.3.B)	E _{Covalent} Atom 2 Hybridization Designation (Table 15.3.B)	S ₂ Atom 1	C ₁	C ₂	q	ζ	E _F (eV)	θ ₁ (°)	θ ₂ (°)	Cal. θ ₃ (°)	Exp. θ ₃ (°)
∠HC ₁ O	2.02241	2.57707	3.9328	15	-13.61806	0.80561 Eq. (15.150)	0.75	1	0.75	0.94470	0			117.02	115.9 (fitted)
∠C ₁ C ₂ H ₁															
∠H ₁ C ₁ C ₂	2.02241	2.66807	4.2269	15	-15.93954 C ₁	0.80561	0.75	1	0.75	1.05822	0			132.29	
∠H ₁ C ₁ C ₂	2.02241	2.60925	4.2269	15	-15.95954 C ₁	0.80561	0.75	1	0.75	1.05822	0			126.09	128.0 (fitted)
∠H ₁ C ₁ C ₂	2.02241	2.60925	4.1312	18	-16.47951 C ₂	0.79597	0.75	1	0.75	1.03725	0			131.32	
∠C ₁ C ₂ H ₁														125.76	
∠C ₁ C ₂ O	2.60925	2.57707	4.2561	18	-17.09534 C ₁	0.79529 Eq. (15.150)	1	1	1	0.79463	-1.63376			127.23	128.0 (fitted)
∠C ₁ O ₁ C ₂	2.57707	2.57707	4.1231	30	-18.22713	0.74646	1	1	1	0.74646	-1.85316			110.69	110.7 (fitted)
∠C ₁ C ₂ C ₃	2.60925	2.68807	4.2426	26	-18.02252	0.75493	1	1	1	0.75927	-1.85216			106.25	106.6 (fitted)
						0.76360								107.01	108.1 (fitted)

THIOPHENE

Thiophene having the formula C_4H_4S comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to an oxygen atom. The two symmetrical carbon-to-oxygen bonds comprise the $C-S-C$ functional group. The 1,3-butdiene moiety
5 comprises $C-C$, $C=C$, and CH functional groups. The CH , $C-C$, and $C=C$ groups are equivalent to the corresponding groups of pyrrole and furan given in the corresponding sections.

The $C-S-C$ functional group of thiophene is solved in a similar manner as that of the $C-N-C$ group of pyrrole and the $C-O-C$ group of furan. The solution of the $C-S-C$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single
10 $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs and the oxygen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the $C-S-C$ -bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1 = 2$ in Eqs. (15.42) and (15.52).

In thiophene, the energy of sulfur is less than the Coulombic energy between the electron
15 and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is $c_2(\text{benzene } C2sp^3 HO) = 0.85252$ to match the double-bond character of the $C2sp^3$ HOs, and the energy matching condition is further determined by the C_2 parameter. Using the energy of S , $E(S) = -10.36001 \text{ eV}$ in Eq. (15.68) and the $C2sp^3$ HO energy of $E(C, 2sp^3) = -15.76868 \text{ eV}$ (Eq. (15.18) corresponding to $s=2$ in Eqs. (15.18-15.20), the
20 hybridization factor C_2 of Eq. (15.52) for the $C-S-C$ -bond MO is

$$C_2(S3p \text{ to aryl-type } C2sp^3 HO) = \frac{E(S, 3p)}{E(C, 2sp^3)} = \frac{-10.36001 \text{ eV}}{-15.76868 \text{ eV}} = 0.65700 \quad (15.153)$$

C_{10} is also given by Eq. (15.153). Furthermore, $\Delta E_{H_1 MO}(AO / HO)$ of the $C-S-C$ -bond MO in Eq. (15.42) and $E_r(\text{atom-atom, } msp^3 AO)$ in Eq. (15.52) are both -0.72457 eV per atom corresponding to -2.89830 eV in total. The energy contribution equivalent to that of
25 a methyl group (Eq. (14.151)) and that of the $C-S$ -bond MO of thiols given in the corresponding section matches the energy of the sulfur atom to the $C2sp^3$ HOs.

The symbols of the functional groups of thiophene are given in Table 15.279. The structure of thiophene is shown in Figure 67. The geometrical (Eqs. (15.1-15.5) and (15.42)),

intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of thiophene are given in Tables 15.280, 15.281, and 15.282, respectively. The total energy of thiophene given in Table 15.283 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.282 corresponding to functional-group composition of the molecule. The 5 bond angle parameters of thiophene determined using Eqs. (15.79-15.108) are given in Table 15.284.

Table 15.279. The symbols of functional groups of thiophene.

Functional Group	Group Symbol
$C_a = C_b$ double bond	$C = C$
$C_b - C_b$	$C - C$
$C_a - S - C_a$	$C - S - C$
CH	CH

Table 15.280. The geometrical bond parameters of thiophene and experimental values [1].

Parameter	C-C Group	C-C Group	C-S-C Group	CH Group
σ (a_0)	1.45103	1.77965	1.74058	1.53380
σ' (a_0)	1.30463	1.33404	1.62766	1.01120
Bond Length $2\sigma'$ (\AA)	1.38076	1.41188	1.72264	1.07021
Exp. Bond Length (\AA)	1.370 (thiophene)	1.423 (thiophene)	1.714 (thiophene)	1.078 (thiophene)
h, c (a_0)	0.63517	1.17792	0.61671	1.15326
e	0.89910	0.74961	0.93513	0.65928

Table 15.281. The MO to HO intercept geometrical bond parameters of thiophene. R_i is an alkyl group and R, R', R'' are H or alkyl groups. E_T is $E_T(\text{atom} - \text{atom}, \text{mip}, \text{AO})$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy C_{2,sp^2} (eV)	r_{bond} (a_0)	r_{bond} (a_0)	$E_{\text{bond}}(C_{2,sp^2})$ (eV) Final	$E(C_{2,sp^2})$ (eV) Final	θ' ($^\circ$)	θ_i ($^\circ$)	θ_i ($^\circ$)	d_i (a_0)	d_i (a_0)
C-H (C, H)	C_s	-1.13380	-0.72457	0	0	-153.47406	0.91771	0.81540	-16.68412	-16.49326	84.49	95.51	44.74	1.08953	0.07833
C-H (C, H)	C_s	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	82.31	97.29	43.14	1.11914	0.10794
$C_s = (H)C_s - C_s(H) = C_s$	C_s	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	91.57	88.43	42.49	1.31226	0.02177
$C_s = C_s(H)(H)C_s = C_s$	C_s	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	136.36	43.64	59.86	0.72857	0.57606
$SC_s = C_s(H)$	C_s	-1.13380	-0.72457	0	0	-153.47406	0.91771	0.81540	-16.68412	-16.49326	137.14	42.86	60.83	0.70653	0.59777
$C_s S - C_s = C_s(H)$	C_s	-1.13380	-0.72457	0	0	-153.47406	0.91771	0.81540	-16.68412	-16.49326	141.52	38.48	55.56	0.89926	0.63840
$C_s S - C_s = C_s(H)$	S'	-0.72457	-0.72457	0	0	-	1.3201	0.83600	-16.27490	-	142.17	37.83	56.24	0.86733	0.66033

Table 15.282. The energy parameters (eV) of functional groups of thiophene.

Parameters	C=C Group	C'-C Group	C-S-C Group	CH Group
n_1	2	1	2	1
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.5	0.5	0.75
C_2	0.85252	1	0.65700	1
C_3	1	1	1	1
C_4	0.85252	0.85252	0.85252	0.91771
S_1	0	0	0	1
S_2	4	2	4	1
S_3	0	0	0	1
C_{ave}	0.5	0.5	0.5	0.75
C_{ave}	0.85252	1	0.65700	1
V_1 (eV)	-104.37986	-33.80733	-96.78916	-39.09538
V_2 (eV)	20.85777	10.19898	16.71820	13.45505
T (eV)	35.96751	9.49831	27.80371	12.74462
V_1 (eV)	-17.98376	-4.74915	-13.90186	-6.37231
E_{HOMO} (eV)	0	-14.63489	0	-14.63489
ΔE_{HOMO} (eV)	-2.26759	-1.85836	-2.89830	-2.26758
E_{LUMO} (eV)	2.26759	-12.77653	2.89830	-12.36731
E_{LUMO} (eV)	-63.27075	-31.63572	-63.27080	-31.63533
E_{LUMO} (eV)	-2.26759	-2.26759	-2.89830	0
E_{LUMO} (eV)	-65.53833	-33.90295	-66.16903	-31.63537
ω (10^5 rad/s)	15.4421	12.3131	10.3184	28.9084
E_{C} (eV)	10.16428	8.10471	6.79173	19.02803
E_{H} (eV)	-0.20668	-0.19095	-0.17058	-0.27301
E_{H} (eV)	0.17897	0.14829	0.08146	0.39427
E_{H} (eV)	[6]	[48]	[41]	[56]
E_{H} (eV)	-0.11720	-0.11680	-0.12983	-0.07387
E_{H} (eV)	0.14803	0.14803	0.14803	0.14803
E_{H} (eV)	-65.77272	-34.01976	-66.42873	-31.71124
E_{H} (eV)	-14.63489	-14.63489	-14.63489	-14.63489
E_{H} (eV)	0	0	0	-13.59844
E_{H} (eV)	7.23317	4.74998	7.88917	3.32988

Table 15.283. The total bond energies of thiophene calculated using the functional group composition and the energies of Table 15.282 compared to the experimental values [2].

Formula	Name	C=C	C-C	C-S-C	CH	Calculated Total Bond Energy (kJ)	Experimental Total Bond Energy (kJ)	Relative Error
C ₄ H ₄ S	Thiophene	2	1	1	4	40,430	40,430	0.0013

Table 15.284. The bond angle parameters of thiophene and experimental values [1]. In the calculation of θ_i , the parameters from the preceding angle were used. E_T is $E_T(\text{atom} - \text{atom}, \text{map}^2, \text{AO})$.

Atom of Angle	$2\phi_1^1$ Bond 1 (ϕ_1)	$2\phi_2^1$ Bond 2 (ϕ_2)	$2\phi_3^1$ Terminal Atom (ϕ_3)	$E_{\text{calculate}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.B)	$E_{\text{calculate}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.B)	ζ_1 Atom 1	ζ_2 Atom 2	ζ_3 Atom 3	C_1	C_2	ζ_4	E_T (eV)	θ_1 (°)	θ_2 (°)	Calc. θ (°)	Exp. θ (°)
$\angle \text{HC}_2\text{S}$	2.02241	3.25533	4.6030	-15.50033	3	-10.36001	S	0.87605 (15.63)	0.76144 (Eq. 15.126)	0.76144 (Eq. 15.126)	0.75	0.76144 (Eq. 15.126)	0.75	0			119.58	119.9 (thiophene)
$\angle \text{C}_2\text{C}_3\text{H}_2$																		
$\angle \text{H}_1\text{C}_1\text{C}_2$	2.02241	2.66807	4.1633	-16.68412	14	-15.95954 C_1	6	0.81549	0.83252	0.83252	0.75	1	0.75	0		119.58	115.84	124.38
$\angle \text{H}_2\text{C}_2\text{C}_1$	2.02241	2.60925	4.1633	-16.68412	14	-15.95954 C_2	6	0.81549	0.83252	0.83252	0.75	1	0.75	0			124.58	124.3 (thiophene)
$\angle \text{H}_1\text{C}_1\text{C}_2$	2.02241	2.60925	4.0825	-17.09334 C_3	16	-16.68412 C_3	14	0.79597	0.81549	0.81549	0.75	1	0.75	0			127.57	
$\angle \text{C}_1\text{C}_2\text{H}_1$																	123.13	
$\angle \text{C}_2\text{C}_3\text{S}$	2.60925	3.25533	4.9809	-17.81791 C_3	27	-10.36001 C_3	S	0.76360 (15.153)	0.65700 (Eq. 15.153)	0.65700 (Eq. 15.153)	1	0.65700 (Eq. 15.153)	1	-0.72457	123.13	113.60	123.27	124.3 (thiophene)
$\angle \text{C}_3\text{NC}_2$	3.25533	3.25533	4.7938	-16.68412	14	-16.68412	14	0.81549	0.81549	0.81549	1	1	1	-1.85836			115.84	115.5 (thiophene)
$\angle \text{C}_2\text{C}_1\text{C}_3$	2.60925	2.66807	4.4159	-16.88873	15	-18.02252	29	0.80561	0.75493	0.75493	1	1	1	-1.85836			94.89	92.2 (thiophene)
														-1.85836			113.60	112.5 (thiophene)

IMIDAZOLE

Imidazole having the formula $C_3H_4N_2$ comprises a conjugated system that is equivalent to pyrrole with one of the conjugated CH groups replaced by a nitrogen atom. The CH , NH , and $C=C$ groups are equivalent to the corresponding groups of pyrrole, furan, and thiophene where present. In addition, the nitrogen substitution creates a $C-N=C$ moiety comprising $C-N$ and $N=C$ functional groups. The $C-N$ bonding is the same as that of a tertiary amine except that the hybridization term c_2 in Eqs. (15.42) and (15.52) is that of the amino group of aniline, $c_2(arylC2sp^3HO\ to\ N) = 0.84665$ (Eq. (15.152)). The hybridization factor provides double-bond character to match the group to the other orbitals of the molecule. $\Delta E_{H_1MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom - atom,msp^3.AO)$ in Eq. (15.52) are both $-0.92918\ eV$ (Eq. (14.513)). This matches the energy of the group to that of the contiguous $N=C$ group wherein $\Delta E_{H_1MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom - atom,msp^3.AO)$ in Eq. (15.52) are both $-0.92918\ eV$ (Eq. (14.513)) per atom of the double bond with aromatic character as in the case of the prior heterocyclic compounds. As in the prior cases of pyrrole, furan, and thiophene, $n_1 = 2$ and C_2 and C_{2o} are the same as $C_2(benzeneC2sp^3HO) = 0.85252$ (Eq. (15.143)) in Eqs. (15.42) and (15.52). To match the energy of the nitrogen to the $C2sp^3\ HO$, c_2 of the $N=C$ -bond MO is also given by Eq. (15.152). These parameters also provide an energy match to the $C-N-C$ group.

As in the case of pyrrole, the $C-N-C$ -bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1 = 2$ in Eqs. (15.42) and (15.52). The hybridization factor $c_2(arylC2sp^3HO\ to\ N) = 0.84665$ (Eq. (15.152)) matches the double-bond character of the $C2sp^3\ HOs$ to the N atom of the NH group, and C_2 and C_{2o} in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143), $C_2(benzeneC2sp^3HO) = 0.85252$. Furthermore, $\Delta E_{H_1MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom - atom,msp^3.AO)$ in Eq. (15.52) are both $-0.92918\ eV$ (Eq. (14.513)) per atom corresponding to $-3.71673\ eV$ in total.

The symbols of the functional groups of imidazole are given in Table 15.285. The structure of imidazole is shown in Figure 68. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of imidazole are given in Tables 15.286, 15.287, and 15.288, respectively. The total energy of imidazole given in Table 15.289 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.288 corresponding to functional-group composition of the molecule. The bond angle parameters of imidazole determined using Eqs. (15.79-15.108) are given in Table 15.290.

10 Table 15.285. The symbols of functional groups of imidazole.

Functional Group	Group Symbol
$C_a = C_b$ double bond	$C = C$
$N_b = C_c$ double bond	$N = C$
$C_b - N_b$	$C - N$
$C_a - N_a - C_c$	$C - N - C$
$N_a H$ group	NH
CH	CH

Table 15.286. The geometrical bond parameters of imidazole and experimental values [1].

Parameter	C=C Group	N=C Group	C-N Group	C-N-C Group	NH Group	CH Group
σ (a_0)	1.45103	1.44926	1.82450	1.43222	1.24428	1.53380
c' (a_0)	1.30463	1.30383	1.35074	1.29614	0.94134	1.01120
Bond Length $2c'$ (\AA)	1.38076	1.37991	1.42956	1.37178	0.996270	1.07021
Exp. Bond Length (\AA)	1.382 (pyrrole)			1.370 (pyrrole)	0.996 (pyrrole)	1.076 (pyrrole)
b_{12} (a_0)	0.63517	0.63276	1.22650	0.60931	0.81370	1.15326
σ	0.89910	0.89965	0.74033	0.90499	0.75653	0.65928

Table 15.287. The MO to HO intercept geometrical bond parameters of imidazole. R_i is an alkyl group and R, R', R'' are H or alkyl groups. E_r is $E_r(\text{atom} - \text{atom}, \text{exp}^2 \text{AO})$.

Bond	Atom	E_r (eV) Bond 1	E_r (eV) Bond 2	E_r (eV) Bond 3	E_r (eV) Bond 4	Final Total Energy ($2, 2p^5$) (eV)	r_{exp} (a_0)	r_{exp} (a_0)	E_{exp} (eV) Final	E_{exp} (eV) Final	θ' ($^\circ$)	θ ($^\circ$)	θ_1 ($^\circ$)	d_1 (a_0)	d_2 (a_0)
$C'-H$ (C_1H)	C_1	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	83.35	96.65	43.94	1.10452	0.09331
$C'-H$ (C_2H)	C_2	-1.13380	-0.46459	0	0	-153.21408	0.91771	0.82840	-16.68414	-16.33327	85.93	94.07	45.77	1.06995	0.09875
$C'-H$ (C_3H)	C_3	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	84.49	95.51	44.47	1.08953	0.07833
$C_2 = (H)C_3 - N_4 = C_1$	C_3	-0.46459	-1.13380	0	0	-153.21408	0.91771	0.82840	-16.42414	-16.23327	90.36	89.64	42.49	1.34347	0.00327
$C_3 = (H)C_2 - N_4 = C_1$	N_4	-0.46459	-0.92918	0	0		0.92084	0.83885	-16.21953		91.32	88.68	43.14	1.33155	0.01919
$C_3 = C_2(H)N_4 = C_1$	C_2	-1.13380	-0.46459	0	0	-153.21408	0.91771	0.82840	-16.42414	-16.23327	137.64	42.36	61.49	0.69250	0.61213
$C_1(H)N_4 - C_2 = C_3(H)$	C_2	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	136.73	43.25	60.35	0.71784	0.58678
$C_1(H)N_4 - C_2 = C_3(H)$	N_4	-0.92918	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	138.54	41.46	61.09	0.69238	0.60176
$N - H$ (N_4H)	N_4	-0.92918	-0.92918	0	0		0.92084	0.81549	-16.68411		138.92	41.08	61.59	0.68147	0.61467
$(H)C_3 - N_4C_2 = C_1(H)$	C_1	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	111.54	62.66	62.90	0.56678	0.37456
$C_3 = (H)C_2N_4 = C_1$	C_3	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	138.92	41.08	61.59	0.68147	0.61467
$C_3 = (H)C_2N_4 = C_1$	C_2	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	137.31	42.69	60.92	0.70446	0.59938
$C_2 = (H)C_3N_4 = C_1$	N_4	-0.92918	-0.46459	0	0		0.92084	0.83885	-16.21953		138.20	41.80	62.08	0.67849	0.62514

Table 15.288. The energy parameters (eV) of functional groups of imidazole.

Parameters	C=C Group	N=C Group	C-N Group	C-N-C Group	NH Group	CH Group
n_1	2	2	1	2	1	1
n_2	0	0	0	0	0	0
n_3	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.5	0.75	0.75
C_2	0.85252	0.85252	1	0.85252	0.91613	1
C_3	1	1	1	1	0.75	1
C_4	0.85252	0.84665	0.84665	0.84665	0.92171	0.91771
C_5	0	0	0	0	1	1
C_6	4	4	2	4	1	1
C_7	0	0	0	0	1	1
C_8	0.5	0.5	0.5	0.5	0.75	0.75
C_9	0.85252	0.85252	1	0.85252	1	1
V_1 (eV)	-104.37086	-103.921756	-32.44864	-106.58684	-39.48897	-39.09538
V_2 (eV)	20.85777	20.87050	10.07285	20.99432	14.45367	13.45505
V_3 (eV)	35.96751	35.85339	8.89248	37.21047	15.86820	12.74462
V_4 (eV)	-17.98376	-17.92770	-4.46524	-18.60523	-7.93410	-6.37251
E_1 (eV)	0	0	-14.63489	0	-14.53414	-14.63489
$\Delta E_{H_{20}}$ (eV)	-2.26759	-1.85836	-0.92918	-3.71673	0	-2.26758
E_{T_1} (eV)	2.26759	1.85836	-13.70571	3.71673	-14.53414	-12.36731
E_{T_2} (eV)	-63.27075	-63.27100	-31.63527	-63.27056	-31.63534	-31.63533
E_T (eV)	-2.26759	-1.85836	-0.92918	-3.71673	0	0
E_{T_1} (eV)	-65.33833	-65.12910	-32.56455	-66.98746	-31.63537	-31.63537
ω (10^5 rad/s)	15.4421	15.4704	21.5113	15.7474	48.7771	28.9084
E_{T_2} (eV)	10.16428	10.18290	14.16571	10.36521	32.10594	19.02803
F_{T_1} (eV)	-0.20668	-0.20558	-0.24248	-0.21333	-0.35462	-0.27301
E_{T_2} (eV)	0.17897	0.20768	0.12944	0.11159	0.40696	0.39427
E_{T_3} (eV)	[6]	[58]	[23]	[12]	[24]	[56]
F_{T_2} (eV)	-0.11720	-0.10174	-0.17775	-0.15754	-0.15115	-0.07587
E_{T_3} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E_{T_4} (eV)	-65.77272	-65.33259	-32.74230	-67.30254	-31.78651	-31.71124
E_{T_5} (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489
E_{T_6} (eV)	0	0	0	0	-13.59844	-13.59844
E_{T_7} (eV)	7.23317	6.79303	3.47353	8.16298	3.51208	3.32988

Table 15.289. The total bond energies of imidazole calculated using the functional group composition and the energies of Table 15.288 compared to the experimental values [2].

Formula	Name	$C=C$	$N=C$	$C-N$	$C-N-C$	NH	CH	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_4H_5N	Imidazole	1	1	1	1	3	3	39.7643	39.7406	-0.0036

Table 15.290. The bond angle parameters of imidazole and experimental values [59]. In the calculation of θ_i , the parameters from the preceding angle were used. E_r is $E_r(\text{atom} - \text{atom}, \text{msp}^\circ \Delta O)$.

Atom/Angle	$2\alpha_1^{\text{cal}}$ Used 1 (α_1)	$2\alpha_2^{\text{cal}}$ Used 2 (α_2)	$2\alpha_3^{\text{cal}}$ Terminal Atom 1 (α_3)	E_r Atom 1 Hybridization Designation (Table 15.38)	E_r Atom 2 Hybridization Designation (Table 15.38)	ζ_1 Atom 1 (Eq. (15.151))	ζ_2 Atom 2 (Eq. (15.151))	ζ_3 Atom 3 (Eq. (15.151))	C_1	C_2	C_3	ζ_4	E_r (eV)	θ_i ($^\circ$)	θ_j ($^\circ$)	θ_k ($^\circ$)	Cal. θ ($^\circ$)	Exp. θ ($^\circ$)
$\angle HC_1N_1$	2.03241	2.59228	4.0166	-14.53414 C_1	-14.53414 N_1	0.91771 (Eq. (15.151))	0.91771 (Eq. (15.151))	0.91771 (Eq. (15.151))	0.75	1	0.75	1.00435	0	120.51	106.63	120.51	120.51	117.4 (midazole)
$\angle C_1C_2H_2$	1.87268	2.59228	3.8987	-14.53414 C_2	-16.40325 H_2	0.84665 (Eq. (15.151))	0.84665 (Eq. (15.151))	0.84665 (Eq. (15.151))	0.75	1	0.75	0.97435	0	120.51	106.63	120.51	120.51	120.9 (midazole)
$\angle HN_1C_1$	2.03241	2.60925	4.2895	-16.88473 C_1	-15.75493 N_1	0.80661 (Eq. (15.151))	0.80661 (Eq. (15.151))	0.80661 (Eq. (15.151))	0.75	1	0.75	1.07196	0	120.51	106.63	120.51	120.51	120.9 (midazole)
$\angle HC_1C_2$	2.03241	2.60925	4.2740	-15.95954 C_2	-14.83575 C_1	0.85252 (Eq. (15.151))	0.85252 (Eq. (15.151))	0.85252 (Eq. (15.151))	0.75	1	0.75	1.07647	0	120.51	106.63	120.51	120.51	120.9 (midazole)
$\angle HN_1C_2$	2.03241	2.59228	3.8471	-15.95954 C_2	-14.53414 N_1	0.87495 (Eq. (15.151))	0.87495 (Eq. (15.151))	0.87495 (Eq. (15.151))	0.75	1	0.75	0.96765	0	120.51	106.63	120.51	120.51	120.9 (midazole)
$\angle N_1C_1H_2$	1.87268	2.59228	4.0661	-14.53414 C_1	-15.76868 H_2	0.84665 (Eq. (15.151))	0.84665 (Eq. (15.151))	0.84665 (Eq. (15.151))	0.75	1	0.75	1.01912	0	120.51	106.63	120.51	120.51	120.9 (midazole)
$\angle HN_1C_2$	2.03241	2.60925	4.1952	-14.53414 C_2	-17.09334 N_1	0.84665 (Eq. (15.151))	0.84665 (Eq. (15.151))	0.84665 (Eq. (15.151))	0.75	1	0.75	0.82131	-1.44915	107.52	107.52	107.52	107.52	106.3 (midazole)
$\angle C_1N_1C_2$	2.59228	2.59228	4.2426	-17.81791 C_2	-17.81791 C_1	0.76560 (Eq. (15.151))	0.76560 (Eq. (15.151))	0.76560 (Eq. (15.151))	1	1	1	0.76560	-1.85835	109.83	109.83	109.83	109.83	107.2 (midazole)
$\angle C_1N_1C_2$	2.60766	2.70148	4.3128	-17.61330 C_2	-17.61330 C_1	0.77247 (Eq. (15.152))	0.77247 (Eq. (15.152))	0.77247 (Eq. (15.152))	1	1	1	0.77247	-1.85836	108.64	108.64	108.64	108.64	107.2 (midazole)
$\angle C_1N_1C_2$	2.60925	2.70148	4.3818	-15.95955 C_2	-16.53414 N_1	0.85252 (Eq. (15.152))	0.85252 (Eq. (15.152))	0.85252 (Eq. (15.152))	1	1	1	0.84958	-1.85836	111.18	111.18	111.18	111.18	109.8 (midazole)
$\angle N_1C_1N_2$	2.59228	2.60766	4.2544	-16.68411 C_1	-16.21953 N_1	0.81549 (Eq. (15.152))	0.81549 (Eq. (15.152))	0.81549 (Eq. (15.152))	1	1	1	0.82717	-1.44915	109.80	109.80	109.80	109.80	111.3 (midazole)

PYRIDINE

Pyridine has the formula C_5H_5N and comprises the benzene molecule with one CH group replaced by a nitrogen atom which gives rise to a $C \equiv N^{3e}$ functional group. The aromatic $C \equiv C^{3e}$ and $C-H$ functional groups are equivalent to those of benzene given in the
 5 Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the $C \equiv N^{3e}$ group which is also aromatic.

As in the case of the aromatic carbons of benzene, each pyridine $C2sp^3$ HO initially has four unpaired electrons. Each $C-H$ bond has two paired electrons with one donated from the H AO and the other from the $C2sp^3$ HO. In pyridine the three $N2p$ electrons are
 10 donated to the aromatic bond. Thus, as in the case of the $C \equiv C^{3e}$ group, each $C \equiv N^{3e}$ bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from the $C2sp^3$ HO and the $N2p$ AO of the participating carbon and nitrogen atoms, respectively.

The solution of the $C \equiv N^{3e}$ functional group comprises the hybridization of the $2s$ and
 15 $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the nitrogen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. The $C \equiv N^{3e}$ -bond MO is solved as a double bond with $n_1 = 2$ in Eqs. (15.42) and (15.147). The hybridization factor $c_2(C2sp^3HO \text{ to } N) = 0.91140$ (Eq. (15.116)) matches the double-bond character of the
 20 $C2sp^3$ HO to the N atom, and C_2 and C_{2a} in Eqs. (15.42) and (15.147) are also given by Eq. (15.116) in order to match the nitrogen to the aromatic $C2sp^3$ HO such that $\Delta E_{H_2MO}(AO/HO) = 0$ in Eq. (15.42). Furthermore, $E_r(atom - atom, msp^3.AO)$ of the $C \equiv N^{3e}$ -bond MO in Eq. (15.147) due to the charge donation from the C and N atoms to the MO is -1.44915 eV corresponding to an energy contribution from each atom that is
 25 equivalent to that of an independent methyl group, -0.72457 eV (Eq. (14.151)). The contributions are also the same as those for a primary amine group as given in the corresponding section. As in the case of benzene, the aromatic $E_r(Group)$ and $E_D(Group)$ are

given by Eqs. (15.146) and (15.147), respectively, with $f_1 = 0.75$. The breakage of the CNC bonds results in three unpaired electrons on the N atom. Thus, the corresponding E_{mag} given by Eq. (15.60) was normalized for the two bonds per atom and for $f_1 = 0.75$ and was subtracted from the total energy of the $C \equiv N$ -bond MO in Eq. (15.147). The pyridine vibrational energies are similar to those of benzene [60]; thus, the value for benzene was used.

The symbols of the functional groups of pyridine are given in Table 15.291. The corresponding designation of the structure is shown in Figure 69. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyridine are given in Tables 15.292, 15.293, and 15.294, respectively. The total energy of pyridine given in Table 15.295 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.294 corresponding to functional-group composition of the molecule. The bond angle parameters of pyridine determined using Eqs. (15.79-15.108) are given in Table 15.296.

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Table 15.291. The symbols of functional groups of pyridine.

Functional Group	Group Symbol
CC (aromatic bond)	$C \equiv C$
CH (aromatic)	CH
$C \equiv N$	$C \equiv N$

Table 15.292. The geometrical bond parameters of pyridine and experimental values [1].

Parameter	C=C Group	C-H Group	C=N Group
a (Å)	1.47348	1.0061	1.47169
c' (Å)	1.31408	1.03299	1.27073
Bond Length $2c'$ (Å)	1.39140	1.09327	1.34489
Exp. Bond Length (Å)	1.394 (pyridine)	1.084 (pyridine)	1.340 (pyridine)
h_{cc} (Å)	0.66540	1.22265	0.74237
ϵ	0.89223	0.64537	0.86345

Table 15.293. The MO to HO intercept geometrical bond parameters of pyridine. E_r is $E_r(\text{atom} - \text{atom}, \text{imp}^2, \text{AO})$.

Bond	Atom	E_r (eV) Bond 1	E_r (eV) Bond 2	E_r (eV) Bond 3	E_r (eV) Bond 4	Final Total Energy C2sp ² (eV)	r_{new} (Å)	r_{new} (Å)	E_{new} (eV) Final	E_{new} (eV) Final	$\bar{E}(\text{C2sp}^2)$ Final	θ^* (°)	θ_1 (°)	θ_2 (°)	d_1 (Å)	d_2 (Å)
C'-H (C', H)	C'	-0.54343	-0.85035	-0.56690	0	-153.57636	0.91771	0.81032	-16.78642	-16.39556	-16.39556	76.35	103.65	40.11	1.22423	0.19124
C'-H (C', H)	C'	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	-16.90248	74.42	105.58	38.84	1.24678	0.21379
(H)C ₃ (H)C ₂ =NC ₁	C ₂	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81032	-16.78642	-16.39556	-16.39556	128.54	51.46	51.65	0.76572	0.50301
(H)C ₃ (H)C ₂ =NC ₁	N	-0.54343	-0.54343	0	0		0.9084	0.85503	-15.91261			130.61	49.39	60.97	0.71418	0.55656
(H)C ₃ =C ₄ (H)N	C ₄	-0.54343	-0.85035	-0.56690	0	-153.57636	0.91771	0.81032	-16.78642	-16.39556	-16.39556	134.85	45.15	59.72	0.74304	0.57165
(H)C ₃ =C ₄ (H)N	C ₃	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.294. The energy parameters (eV) of functional groups of pyridine.

Parameters	C-C Group	CH Group	C=N Group
f_1	0.75	1	0.75
n_1	2	1	2
n_2	0	0	0
n_3	0	0	0
C_1	0.5	0.75	0.5
C_2	0.85252	1	0.91140
C_3	1	1	1
C_4	0.85252	0.91771	0.91140
C_5	0	1	0
C_6	3	1	3
C_7	0	1	0
C_{10}	0.5	0.75	0.5
C_{12}	0.85252	1	0.91140
V_1 (eV)	-101.12679	-37.10024	-102.01431
V_2 (eV)	20.69825	13.17125	21.41410
T (eV)	34.31559	11.58941	34.65890
V_e (eV)	-17.15779	-5.79470	-17.32945
$E_{1,ex(10)}$ (eV)	0	-14.63489	0
$\Delta E_{H,10}$ (eV)	0	-1.13379	0
$E_{1,ex(10)}$ (eV)	0	-13.50110	0
$E_{1,ex(10)}$ (eV)	-63.27075	-31.63539	-63.27076
$E_{1,ex(10)}$ (eV)	-2.26759	-0.56690	-1.44915
$E_{1,ex(10)}$ (eV)	-65.53833	-32.20226	-64.71988
ω (10^3 rad/s)	49.7272	26.4826	43.6311
$E_{1,ex(10)}$ (eV)	32.73133	17.43132	28.71875
$E_{1,ex(10)}$ (eV)	-0.35806	-0.26130	-0.33540
$E_{1,ex(10)}$ (eV)	0.19649	0.35332	0.19649
$E_{1,ex(10)}$ (eV)	-0.25982	-0.08364	-0.23715
$E_{1,ex(10)}$ (eV)	0.14803	0.14803	0.09457
$E_{1,ex(10)}$ (eV)	-49.54347	-32.28590	-48.82472
$E_{1,ex(10)}$ (eV)	-14.63489	-14.63489	-14.63489
$E_{1,ex(10)}$ (eV)	0	-13.59844	0
$E_{1,ex(10)}$ (eV)	5.63881	3.90454	4.92005

Table 15.295. The total bond energies of pyridine calculated using the functional group composition and the energies of Table 15.294 compared to the experimental values [2].

Formula	Name	$\text{C}=\text{C}$	$\text{C}-\text{H}$	$\text{C}=\text{N}$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$\text{C}_5\text{H}_5\text{N}$	Pyridine	4	5	2	51.9192	51.8792	-0.00075

Table 15.296. The bond angle parameters of pyridine and experimental values [1]. E_f is $E_f(\text{atom} - \text{atom}, \text{exp. AO})$.

Atoms of Angle	$2c'$ Atom 1	$2c'$ Atom 2	$2c'$ Atom 3	$E_{\text{functional}}$ Atom 1	$E_{\text{functional}}$ Atom 2	Hybridization Designation Atom 2	c_2 Atom 1	c_2 Atom 2	c_1	c_2	c_1	ζ_1	E_f (eV)	θ_1 (°)	θ_2 (°)	θ_3 (°)	Cal. θ (°)	Exp. θ (°)
$\angle(\text{C}'\text{C}'\text{C}')$ (aromatic)	2.63936	2.63936	4.5335	-17.17218	-17.17218	20	0.79332	0.79332	1	1	1	0.79332	-1.85336				120.19	120 [90-33] (benzene) 112.3 (pyridine)
$\angle(\text{C}'\text{C}'\text{H})$ (aromatic)																	120.19	120 [90-33] (benzene) 112.3 (pyridine)
$\angle(\text{H}'\text{C}'\text{N})$	2.06598	2.54147	3.9497	-14.53414	-14.53414	N	0.91771	0.91740 E_f (15.116)	0.75	1	0.75	0.99312	0				117.65	115.9 (pyridine)
$\angle(\text{N}'\text{C}'\text{C}_s)$	2.54147	2.63936	4.5607	-14.53414	-16.53644 C_s	12	0.91740 E_f (15.116)	0.82377	1	1	1	0.86734	-1.44915				123.76	123.9 (pyridine)
$\angle(\text{C}'\text{N}'\text{C}_s)$	2.54147	2.54147	4.3359	-17.71560	-17.71560	24	0.76001	0.76001	1	1	1	0.76001	-1.85336				117.09	116.8 (pyridine)

PYRIMIDINE

Pyrimidine has the formula $C_4H_4N_2$ and comprises the pyridine molecule with one additional CH group replaced by a nitrogen atom which gives rise to a second $C=N^{3e}$ functional group that is equivalent to that of pyridine given in the corresponding section. The aromatic $C=C^{3e}$ and $C-H$ functional groups are also equivalent to those of pyridine and benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the $C=N^{3e}$ group which is also aromatic.

The symbols of the functional groups of pyrimidine are given in Table 15.297. The corresponding designation of the structure is shown in Figure 70. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyrimidine are given in Tables 15.298, 15.299, and 15.300, respectively. The total energy of pyrimidine given in Table 15.301 was calculated as the sum over the integer multiple of each $E_D(\text{group})$ of Table 15.300 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrimidine determined using Eqs. (15.79-15.108) are given in Table 15.302.

Table 15.297. The symbols of functional groups of pyrimidine.

Functional Group	Group Symbol
CC (aromatic bond)	$C=C^{3e}$
CH (aromatic)	CH
$C_{a,b,d}^{3e}=N$	$C=N^{3e}$

Table 15.298. The geometrical bond parameters of pyrimidine and experimental values [1].

Parameter	C=C Group	CH Group	C=N Group
a (Å)	1.47348	1.60061	1.47169
c (Å)	1.31468	1.03259	1.27073
Bond Length $2c$ (Å)	1.39140	1.09327	1.34489
Exp. Bond Length (Å)	1.393 (pyrimidine)	1.084 (pyridine)	1.340 (pyrimidine)
b, c (Å)	0.66540	1.22265	0.74237
ϵ	0.89723	0.64537	0.86345

Table 15.299. The MO to HO intercept (geometrical bond parameters of pyrimidine. E_r is E_r (atom - atom, map^3 , AO).

Bond	Atom	E_r (eV) Bond 1	E_r (eV) Bond 2	E_r (eV) Bond 3	E_r (eV) Bond 4	Final Total Energy $C2_{sp^3}$ (eV)	r_{C-H} (Å)	r_{C-N} (Å)	r_{C-C} (Å)	$E(C2_{sp^3})$ (eV) Final	θ^* (°)	θ_1 (°)	θ_2 (°)	d_1 (Å)	d_2 (Å)
C-H (C, H)	C ₂	-0.54343	-0.54343	-0.56690	0	-153.26945	0.91771	0.82562	-16.47951	-16.28864	78.27	101.73	41.39	1.20084	0.16785
C-H (C ₂ , H)	C ₃	-0.54343	-0.54343	-0.56690	0	-153.27636	0.91771	0.81032	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
C-H (C ₂ , H)	C ₄	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21279
(H)C ₂ (H)C ₃ =N ₁ C ₄	C ₅	-0.85035	-0.84343	-0.56690	0	-153.27636	0.91771	0.81032	-16.78642	-16.59556	122.54	51.46	51.65	0.76572	0.50501
(H)C ₂ (H)C ₃ =N ₁ C ₄	N ₁	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
(H)C ₂ (H)C ₃ =N ₁ C ₄	N ₂	-0.54343	-0.54343	-0.56690	0	-153.26945	0.91771	0.82562	-16.47951	-16.28865	129.26	50.74	59.64	0.74824	0.52249
(H)C ₂ (H)C ₃ =N ₁ C ₄	C ₅	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
(H)C ₂ (H)C ₃ =N ₁ C ₄	C ₆	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	42.76	58.98	0.73935	0.55533
(H)C ₂ (H)C ₃ =N ₁ C ₄	C ₇	-0.85035	-0.84343	-0.56690	0	-153.27636	0.91771	0.81032	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165

Table 15.300. The energy parameters (eV) of functional groups of pyrimidine.

Parameters	C=C Group	C-H Group	C=N Group
f_1	0.75	1	0.75
n_1	2	1	2
n_2	0	0	0
n_3	0	0	0
C_1	0.5	0.75	0.5
C_2	0.85252	1	0.91140
C_3	1	1	1
C_4	0.85252	0.91771	0.91140
C_5	0	1	0
C_6	3	1	3
C_7	0	1	0
C_{12}	0.5	0.75	0.5
C_{13}	0.85252	1	0.91140
V_1 (eV)	-101.12679	-37.10024	-102.01431
V_2 (eV)	20.69825	13.17125	21.41410
T (eV)	34.31559	11.58941	34.65890
V_3 (eV)	-17.15779	-5.79470	-17.32945
$E_{120\text{ mJ}}$ (eV)	0	-14.63489	0
$\Delta E_{120\text{ mJ}}$ (eV)	0	-1.13379	0
$E_{120\text{ mJ}}$ (eV)	0	-13.50110	0
$E_{120\text{ mJ}}$ (eV)	-63.27075	-31.63539	-63.27076
$E_{120\text{ mJ}}$ (eV)	-2.26759	-0.56690	-1.44915
$E_{120\text{ mJ}}$ (eV)	-65.53833	-32.20226	-64.71988
ω (10^{11} rad/s)	49.7272	26.4826	43.6311
$E_{120\text{ mJ}}$ (eV)	32.73133	17.43132	28.71875
$E_{120\text{ mJ}}$ (eV)	-0.35806	-0.26130	-0.33540
$E_{120\text{ mJ}}$ (eV)	0.19649	0.35532	0.19649
$E_{120\text{ mJ}}$ (eV)	[49]	Eq. (13.458)	[49]
$E_{120\text{ mJ}}$ (eV)	-0.25982	-0.08304	-0.23715
$E_{120\text{ mJ}}$ (eV)	0.14803	0.14803	0.09457
$E_{120\text{ mJ}}$ (eV)	-49.54347	-32.28590	-48.82472
$E_{120\text{ mJ}}$ (eV)	-14.63489	-14.63489	-14.63489
$E_{120\text{ mJ}}$ (eV)	0	-13.59844	0
$E_{120\text{ mJ}}$ (eV)	5.63881	3.90454	4.92005

Table 15.301. The total bond energies of pyrimidine calculated using the functional group composition and the energies of Table 15.300 compared to the experimental values [2].

Formula	Name	C=C		C-H		C=N		Calculated	Experimental	Relative Error
C ₄ H ₄ N ₂	Pyrimidine	2	2	4	4	4	4	46.51597	46.51794	-0.00195

Table 15.302. The bond angle parameters of pyrimidine and experimental values [1]. E_r is $E_f(atom - atom, nsp^2, AO)$.

Atom or Angle	$2c_1$ (σ_1)	$2c_2$ (σ_2)	$2c_3$ (σ_3)	$E_{\text{functional}}$ Atom 1 (σ_1)	Atom 1 Hybridization Designation (Table 15.3B)	$E_{\text{functional}}$ Atom 2 (σ_2)	Atom 2 Hybridization Designation (Table 15.3B)	c_1 Atom 1	c_2 Atom 2	c_3 Atom 3	C_1	C_2	C_3	c_4	c_5	E_r (eV)	θ_1 (°)	θ_2 (°)	θ_3 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C' C''$ (aromatic)	2.62936	2.62936	4.5385	-17.17218	20	-17.17218	20	0.79332	0.79272		1	1	1	1	1	-1.83836				120.19	120 [50-32] (benzene) 118.3 (pyridine) 111.5 (pyridine)
$\angle C' H$ (aromatic)																		120.19		119.91	120 [50-32] (benzene) 111.5 (pyridine)
$\angle H C' N$	2.04598	2.54147	3.9497	-14.82275	1	-14.53414	N	0.91771	0.91140 (13.116)	0.75	0.75	1	1	1	1	0				117.65	115.9 (pyridine)
$\angle N C' C'$	2.54147	2.62936	4.5607	-14.53414	N	-16.52644	13	0.91140 (13.116)	0.82327	1	1	1	1	1	1	-1.44915				121.76	121.9 (pyridine)
$\angle C' N C'$	2.54147	2.54147	4.3359	-17.71560	24	-17.71560	24	0.76801	0.76801	1	1	1	1	1	1	-1.85836				117.00	115.3 (pyrimidine)
$\angle N C' N$	2.54147	2.54147	4.5826	-15.55033	3	-15.55033	3	0.87495	0.87495	1	1	1	1	1	1	-1.83836				124.71	127.6 (pyrimidine)

PYRAZINE

Pyrazine has the formula $C_4H_4N_2$ and comprises the pyrimidine molecule with para rather than ortho aromatic nitrogen atoms. The $C \overset{3e}{=} N$ functional group is equivalent to that of pyrimidine and pyridine given in the corresponding sections. The aromatic $C \overset{3e}{=} C$ and 5 $C-H$ functional groups are also equivalent to those of pyrimidine, pyridine, and benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the $C \overset{3e}{=} N$ group which is also aromatic.

The symbols of the functional groups of pyrazine are given in Table 15.303. The corresponding designation of the structure is shown in Figure 71. The geometrical (Eqs. 10 (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyrazine are given in Tables 15.304, 15.305, and 15.306, respectively. The total energy of pyrazine given in Table 15.307 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.306 corresponding to functional-group composition of the molecule. The bond angle parameters 15 of pyrazine determined using Eqs. (15.79-15.108) are given in Table 15.308.

Table 15.303. The symbols of functional groups of pyrazine.

Functional Group	Group Symbol
CC (aromatic bond)	$C \overset{3e}{=} C$
CH (aromatic)	CH
$C \overset{3e}{=} N$	$C \overset{3e}{=} N$

Table 15.304. The geometrical bond parameters of pyrazine and experimental values [1].

Parameter	C=C Group	CH Group	C=N Group
a (a_0)	1.47348	1.60061	1.47169
c' (a_0)	1.31466	1.03299	1.27073
Bond Length $2c'$ (\AA)	1.39140	1.09327	1.34489
Exp. Bond Length (\AA)	1.339 (pyrazine)	1.115 (pyrazine)	1.403 (pyrazine)
a, c (a_0)	0.66340	1.22265	0.74237
σ	0.89223	0.64537	0.86345

Table 15.305. The MO to HO intercept geometrical bond parameters of pyrazine. E_T is $E_T(\text{atom} - \text{atom}, \text{exp}^1, \text{AO})$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy C2sp ² (eV)	r_{exp} (a_0)	ϵ_{exp} (C2sp ²) (eV) Final	$E(\text{C2sp}^2)$ (eV) Final	θ^* (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
C-H (C ₂ H)	C ₂	-0.54343	-0.85015	-0.56690	0	-153.57636	0.91771	-16.78642	-16.59556	76.35	103.65	40.11	1.22433	0.19124
(H)C ₂ (H)C ₃ =NC ₄	C ₃	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.59501
(H)C ₂ (H)C ₃ =NC ₄	N	-0.54343	-0.85035	0	0		0.52064	-15.91261		130.61	49.39	60.97	0.71418	0.55656
N(H)C ₂ =C ₃ (H)N	C ₃	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	-16.78642	-16.59556	134.85	45.15	59.72	0.74504	0.57163

Table 15.206. The energy parameters (eV) of functional groups of pyrazine.

Parameters	C=C Group	CH Group	C=N Group
f_1	0.75	1	0.75
n_1	2	1	2
n_2	0	0	0
n_3	0	0	0
C_1	0.5	0.75	0.5
C_2	0.85252	1	0.91140
C_3	1	1	1
C_4	0.85252	0.91771	0.91140
C_5	0	1	0
C_6	3	1	3
C_7	0	1	0
C_8	0.5	0.75	0.5
C_{10}	0.85252	1	0.91140
V_1 (eV)	-101.12679	-37.10024	-102.01431
V_2 (eV)	20.69825	13.17125	21.41410
V_3 (eV)	34.31559	11.58941	34.65890
V_4 (eV)	-17.15779	-5.79470	-17.32945
E (eV)	0	-14.63489	0
$\Delta E_{1,2,3,4}$ (eV)	0	-1.13379	0
E_T (eV)	0	-13.50110	0
E_T (eV)	-43.27075	-31.63559	-63.27076
E_T (eV)	-2.26759	-0.56690	-1.44915
E_T (eV)	-65.53833	-32.20226	-64.71988
ω (10^{11} rad/s)	49.7272	26.4826	43.6311
E_F (eV)	32.73133	17.43132	28.71875
E_D (eV)	-0.35806	-0.26130	-0.33540
$E_{F_{max}}$ (eV)	0.19649	0.35532	0.19649
$E_{F_{min}}$ (eV)	[49]	E_0 (13.458)	[49]
$E_{F_{max}}$ (eV)	-0.25982	-0.08364	-0.23715
$E_{F_{min}}$ (eV)	0.14803	0.14803	0.09457
E_T (eV)	-49.54347	-32.28590	-48.87472
$E_{F_{max}}$ (eV)	-14.63489	-14.63489	-14.63489
$E_{F_{min}}$ (eV)	0	-13.59844	0
E_T (eV)	5.63881	3.90454	4.92005

Table 15.307. The total bond energies of pyrazine calculated using the functional group composition and the energies of Table 15.306 compared to the experimental values [2].

Formula	Name	$\Sigma C=C$	$\Sigma C-H$	$\Sigma C=N$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_4H_4N_2$	Pyrazine	2	4	4	46.51397	46.51380	0.00015

Table 15.308. The bond angle parameters of pyrazine and experimental values [1]. E_T is $E_T(atom-atom,exp, AO)$.

Atom of Angle	$2c_1$ Bond 1 (σ_1)	$2c_2$ Bond 2 (σ_2)	$2c_3$ Terminal Atom (σ_3)	$E_{\text{calculated}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{\text{calculated}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	q_1	q_2	E_T (eV)	θ_1 ($^\circ$)	θ_2 ($^\circ$)	θ_3 ($^\circ$)	Cal. θ ($^\circ$)	Exp. θ ($^\circ$)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	20	-17.17218	20	0.79232	0.79232	1	1	1	1	-1.83816					120 [16-52] (benzene) 118.3 (pyridine) 118.5 (pyridine)
$\angle CCH$ (aromatic)																			120 [16-52] (pyridine) 121.3 (pyridine)
$\angle MCN$	2.60598	2.54147	3.9497	-14.82375	1	-14.83414	N	0.91771	0.91140 E_q (15.116)	0.75	1	0.75	0.99312	0					119.91 (pyridine)
$\angle C'CH$																			117.65 (pyridine)
$\angle MCC'$	3.54147	2.62936	4.4045	-14.83414	N	-17.09334	7	0.91140 E_q (15.116)	0.79597	1	1	1	1	-1.44915					123.9 (pyrazine) 125.54 (pyrazine)
$\angle C'NC'$	2.54147	2.54147	4.3359	-17.71560	24	-17.71560	24	0.76801	0.76801	1	1	1	1	-1.83836					116.81 (pyrazine) 116.8 (pyridine)

QUINOLINE

Quinoline has the formula C_9H_7N and comprises the naphthalene molecule with one CH group replaced by a nitrogen atom which gives rise to a $C \overset{3e}{=} N$ functional group. The aromatic $C \overset{3e}{=} C$ and $C-H$ functional groups are equivalent to those of naphthalene given in the corresponding section with the aromaticity maintained by the electrons from nitrogen in the $C \overset{3e}{=} N$ group which is also aromatic. The $C-C$ functional group is also equivalent to that of naphthalene. The bonding in quinoline can be further considered as a linear combination of the naphthalene and pyridine groups wherein the $C \overset{3e}{=} N$ group is equivalent to that of pyridine, pyrimidine, and pyrazine as given in the corresponding sections.

The symbols of the functional groups of quinoline are given in Table 15.309. The corresponding designation of the structure is shown in Figure 72. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of quinoline are given in Tables 15.310, 15.311, and 15.312, respectively. The total energy of quinoline given in Table 15.313 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.312 corresponding to functional-group composition of the molecule. The bond angle parameters of quinoline determined using Eqs. (15.79-15.108) are given in Table 15.314.

Table 15.309. The symbols of functional groups of quinoline.

Functional Group	Group Symbol
CC (aromatic bond)	$C \overset{3e}{=} C$
CH (aromatic)	CH
$C_b - C_h$ (bridging bond)	$C - C$
$C_{a,d} \overset{3e}{=} N$	$C \overset{3e}{=} N$

Table 15.3.10. The geometrical bond parameters of quinoline and experimental values [1].

Parameter	C=C Group	C-H Group	C-C Group	C=N Group
a (a_0)	1.47348	1.60061	1.75607	1.47169
c' (a_0)	1.31468	1.03299	1.32517	1.27073
Bond Length $2c'$ (\AA)	1.39140	1.09227	1.40250	1.34489
Exp. Bond Length (\AA)	1.40 (avg.) (naphthalene)	1.101 (benzene)	1.42 (naphthalene)	1.340 (pyridine)
b, c (a_0)	0.66540	1.22265	1.15226	0.74237
e	0.89223	0.64537	0.75462	0.86345

Table 15.3.11. The MO to HO intercept geometrical bond parameters of quinoline. E_r is $E_r(\text{atom} - \text{atom}, \text{asp}^3 \text{AO})$.

Bond	Atom	E_r (eV) Bond 1	E_r (eV) Bond 2	E_r (eV) Bond 3	E_r (eV) Bond 4	Final Total Energy C_{2sp^3} (eV)	r_{bond} (a_0)	r_{bond} (a_0)	E_{bond} (eV) Final	$E(C_{2sp^3})$ (eV) Final	θ°	θ_1°	θ_2°	d_1 (a_0)	d_2 (a_0)
C-H (C_1 -H)	C ₁	-0.85035	-0.44343	-0.36690	0	-153.17636	0.91771	0.81052	-16.78642	-16.59556	76.35	103.65	40.11	1.23523	0.19174
C-H (C_2 -H)	C ₂	-0.85035	-0.44343	-0.36690	0	-153.18327	0.91771	0.79597	-17.09334	-16.50248	74.42	105.58	38.84	1.24678	0.21379
N(H)(C ₂ =C ₃)(H)	C ₃	-0.85035	-0.44343	-0.36690	0	-153.17636	0.91771	0.81052	-16.78642	-16.59556	134.85	45.15	58.72	0.74304	0.57165
(H)(C ₂ =C ₃)(H)	C ₃	-0.85035	-0.44343	-0.36690	0	-153.18327	0.91771	0.79597	-17.09334	-16.50248	134.24	45.76	58.98	0.75935	0.55553
(H)(C ₂ =C ₃)(C ₄ =C ₅)	C ₄	-0.85035	-0.44343	-0.36690	0	-153.19983	0.91771	0.80929	-16.60949	-16.61903	134.81	45.19	58.65	0.74430	0.57038
N(C ₂)C ₃ =C ₄	C ₄	-0.85035	-0.44343	-0.36690	0	-153.19983	0.91771	0.80929	-16.60949	-16.61903	135.42	44.58	60.42	0.72743	0.58725
C ₄ (H)(C ₅ =N)	C ₅	-0.85035	-0.44343	-0.36690	0	-153.17636	0.91771	0.81052	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50501
C ₄ (H)(C ₅ =N)	N	-0.54343	-0.44343	0	0		0.80884	0.85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
C ₄ (C ₅)C ₆ =N	C ₆	-0.85035	-0.44343	-0.36690	0	-153.19983	0.91771	0.80929	-16.60949	-16.61903	128.21	50.79	59.38	0.74960	0.52113
(H)(C ₅)C ₆ =N	C ₆	-0.85035	-0.44343	-0.36690	0	-153.19983	0.91771	0.80929	-16.60949	-16.61903	95.01	84.99	44.41	1.25451	0.07066
N(C ₅)C ₆ =C ₇	C ₇	-0.85035	-0.44343	-0.36690	0	-153.19983	0.91771	0.80929	-16.60949	-16.61903	96.31	83.69	45.33	1.23456	0.09061

Table 15.312. The energy parameters (eV) of functional groups of quincline.

Parameters	C=C Group	CH Group	C-C Group	C=N Group
f_1	0.75	1	1	0.75
n_1	2	1	1	2
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.75	0.5	0.5
C_2	0.85252	1	1	0.91140
C_3	1	1	1	1
S_1	0.85252	0.91771	0.85252	0.91140
S_2	0	1	0	0
S_3	3	1	2	3
S_4	0	1	0	0
C_{1a}	0.5	0.75	0.5	0.5
C_{1b}	0.85252	1	1	0.91140
V_1 (eV)	-101.12679	-37.10024	-34.43791	-102.01431
V_2 (eV)	20.69825	13.17125	10.26723	21.41410
T_1 (eV)	34.31559	11.58941	9.80539	34.65890
V_{π} (eV)	-17.15779	-5.79470	-4.90270	-17.32945
$E_{1,10}^{\pi}$ (eV)	0	-14.63489	-14.63489	0
$\Delta E_{1,10}^{\pi}$ (eV)	0	-1.13379	-1.13379	0
$E_{1,10}^{\pi}$ (eV)	0	-13.50110	-13.50110	0
$E_{1,10}^{\pi}$ (eV)	-63.27075	-31.63539	-31.63539	-63.27076
$E_{1,10}^{\pi}$ (eV)	-2.26759	-0.56690	-0.56690	-1.44915
$E_{1,10}^{\pi}$ (eV)	-45.55833	-32.20226	-32.20226	-44.71988
ω (10^{14} rad/s)	49.7212	26.4826	23.6343	43.6311
$E_{1,10}^{\pi}$ (eV)	32.73133	17.43132	15.55648	28.71875
$E_{1,10}^{\pi}$ (eV)	-0.35806	-0.26130	-0.25127	-0.33540
$E_{1,10}^{\pi}$ (eV)	0.19649	0.35532	0.12312	0.19649
$E_{1,10}^{\pi}$ (eV)	[49]	$E_{1,10}^{\pi}$ (13.458)	[2]	[49]
$E_{1,10}^{\pi}$ (eV)	-0.25982	-0.08364	-0.18971	-0.23715
$E_{1,10}^{\pi}$ (eV)	0.14803	0.14803	0.14803	0.09457
$E_{1,10}^{\pi}$ (eV)	-49.54347	-32.28590	-32.39198	-48.82472
$E_{1,10}^{\pi}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{1,10}^{\pi}$ (eV)	0	-13.59844	0	0
$E_{1,10}^{\pi}$ (eV)	5.63881	3.90454	3.12220	4.92005

Table 15.13. The total bond energies of quinoline calculated using the functional group composition and the energies of Table 15.312 compared to the experimental values [2].

Formula	Name	2^1 $C=C$	2^2 $C-C$	2^3 $C-H$	Group	Total Bond Energy (eV)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_4	Quinoline	8	7	1	2	85.4053	85.4857	0.0078	

Table 15314. The bond angle parameters of quinoline and experimental values [1]. E_r is $E_r(\text{atom} \rightarrow \text{atom}, \text{in sp}^1 \text{AO})$.

Atoms of Angle	$2C'$ Bond 1 (α_1)	$2C'$ Bond 2 (α_2)	$2C'$ Terminal Atom (α_3)	$E_{\text{Terminal Atom 1}}^{\text{Coulombic}}$ (e_1)	$E_{\text{Terminal Atom 2}}^{\text{Coulombic}}$ (e_2)	$E_{\text{Hybridization Disagreement}}$ (Table 15.3B)	$E_{\text{Hybridization Disagreement}}$ (Table 15.3B)	C_1	C_2	ζ	E_T (eV)	θ_1 ($^\circ$)	θ_2 ($^\circ$)	θ_3 ($^\circ$)	Cal. θ ($^\circ$)	Exp. θ ($^\circ$)
$\angle C C C$	2.65936	2.65034	4.5385	-17.17218	20	-17.17218	20	0.79232	1	1	-1.85316				119.40	119.4 (naphthalene)
$\angle C C' H$												119.40				
$\angle C' C' H$	2.54147	2.54147	4.3118	-17.43216	22	-17.43216	24	0.78050	1	1	-1.85316				119.10	

ISOQUINOLINE

Isoquinoline has the formula C_9H_7N and comprises the naphthalene molecule with one CH group replaced by a nitrogen atom which gives rise to a $C \equiv N^{3e}$ functional group. Isoquinoline is also equivalent to quinoline with the nitrogen in the meta rather than the ortho position relative to the benzene ring of the molecule. The aromatic $C \equiv C^{3e}$ and $C-H$ functional groups are equivalent to those of naphthalene given in the corresponding section with the aromaticity maintained by the electrons from nitrogen in the $C \equiv N^{3e}$ group which is also aromatic. The $C-C$ functional group is also equivalent to that of naphthalene. The bonding in isoquinoline can be further considered as a linear combination of the naphthalene and pyridine groups wherein the $C \equiv N^{3e}$ group is equivalent to that of pyridine, pyrimidine, pyrazine, and quinoline as given in the corresponding sections.

The symbols of the functional groups of isoquinoline are given in Table 15.315. The corresponding designation of the structure is shown in Figure 73. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of isoquinoline are given in Tables 15.316, 15.317, and 15.318, respectively. The total energy of isoquinoline given in Table 15.319 was calculated as the sum over the integer multiple of each $E_D(Grp)$ of Table 15.318 corresponding to functional-group composition of the molecule. The bond angle parameters of isoquinoline determined using Eqs. (15.79-15.108) are given in Table 15.320.

Table 15.315. The symbols of functional groups of isoquinoline.

Functional Group	Group Symbol
CC (aromatic bond)	$C \equiv C^{3e}$
CH (aromatic)	CH
$C_b - C_b$ (bridging bond)	$C - C$
$C_{a,d} \equiv N^{3e}$	$C \equiv N^{3e}$

Table 15.3.16. The geometrical bond parameters of isoquinoline and experimental values [1].

Parameter	C=C Group	CH Group	C-C Group	C=N Group
σ (Å)	1.47348	1.00661	1.75607	1.47169
σ' (Å)	1.31468	1.03299	1.37517	1.27073
Bond Length 2c' (Å)	1.39140	1.09327	1.40250	1.34489
Exp. Bond Length (Å)	1.40 (avg.) (naphthalene)	1.101 (benzene)	1.42 (naphthalene)	1.340 (pyridine)
h, c (Å)	0.66540	1.22265	1.15226	0.74237
a	0.89723	0.64537	0.75462	0.86345

Table 15.3.17. The MO to HO intercept geometrical bond parameters of isoquinoline. E_p is $E_p(\text{atom} - \text{atom}, \text{m.u.}^2 \text{AO})$.

Bond	Atom	E_p (eV) Bond 1	E_p (eV) Bond 2	E_p (eV) Bond 3	E_p (eV) Bond 4	Final Total Energy C_{2sp} (eV)	r_{bond} (Å)	r_{bond} (Å)	E_{bond} (eV) Final	E_{bond} (eV) Final	θ (°)	θ_1 (°)	θ_2 (°)	d_1 (Å)	d_2 (Å)
C-H (C,H)	C _u	-0.85035	-0.44343	-0.36690	0	-153.7636	0.91771	0.81032	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
C-H (C,H)	C _u	-0.85035	-0.44343	-0.36690	0	-153.7636	0.91771	0.81032	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
C-H (C,H)	C _u	-0.85035	-0.44343	-0.36690	0	-153.88327	0.91771	0.79597	-17.09314	-16.90248	74.42	105.58	38.84	1.24678	0.21379
N(H)C _u =C _u	C _u	-0.85035	-0.44343	-0.36690	0	-153.7636	0.91771	0.81032	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165
N(H)C _u =C _u	C _u	-0.85035	-0.44343	-0.36690	0	-153.7636	0.91771	0.79597	-17.09314	-16.90248	134.24	45.76	58.98	0.75935	0.55533
(H)C _u (C _u)C _u =C _u	C _u	-0.85035	-0.44343	-0.36690	0	-153.88327	0.91771	0.80939	-16.80989	-16.61903	134.81	45.19	59.66	0.74430	0.57038
(H)C _u (C _u)C _u =C _u	C _u	-0.85035	-0.44343	-0.36690	0	-153.7636	0.91771	0.81032	-16.78642	-16.59556	128.34	51.46	58.65	0.76572	0.50501
C _u (H)C _u =N	N	-0.54343	-0.44343	0	0	-153.7636	0.91084	0.85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
C _u (H)C _u =N	C _u	-0.85035	-0.44343	-0.36690	0	-153.88327	0.91771	0.80939	-16.80989	-16.61903	93.01	84.99	44.41	1.23451	0.07066

Table 15.318. The energy parameters (eV) of functional groups of isoquinoline.

Parameters	C=C Group	C-H Group	C-C Group	C=N Group
f_1	0.75	1	1	0.75
n_1	2	1	1	2
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.75	0.5	0.5
C_2	0.85252	1	1	0.91140
S_1	1	1	1	1
S_2	0.85252	0.91771	0.85252	0.91140
S_3	0	1	0	0
S_4	3	1	2	3
S_5	0	1	0	0
C_{1n}	0.5	0.75	0.5	0.5
C_{2n}	0.85252	1	1	0.91140
V_1 (eV)	-101.12679	-37.10024	-34.3791	-102.01431
V_2 (eV)	20.69825	13.17125	10.26723	21.41410
T (eV)	34.31559	11.58941	9.80539	34.63890
V_n (eV)	-17.15719	-5.79470	-4.90270	-17.32945
$E(100\text{ m})$ (eV)	0	-14.63489	-14.63489	0
$\Delta E_{n,100}$ (eV)	0	-1.13379	-1.13379	0
$E_p(100\text{ m})$ (eV)	0	-13.50110	-13.50110	0
$E_p(100\text{ m})$ (eV)	-63.27075	-31.63539	-31.63529	-63.27076
$E_p(100\text{ m})$ (eV)	-2.26759	-0.56690	-0.56690	-1.44915
$E_p(100\text{ m})$ (eV)	-65.53833	-32.20226	-32.20226	-64.71988
ω (10^9 rad/s)	49.7272	26.4826	23.6343	43.6311
E_c (eV)	32.73133	17.43132	15.55648	28.71875
E_v (eV)	-0.35806	-0.26130	-0.25127	-0.33540
E_{100} (eV)	0.19649	0.35532	0.12312	0.19649
E_{100} (eV)	-0.25982	-0.08364	-0.18971	-0.23715
E_{100} (eV)	0.14803	0.14803	0.14803	0.09457
$E_p(100\text{ m})$ (eV)	-49.54347	-32.28590	-32.39198	-48.82472
$E_{100}(100\text{ m})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{100}(100\text{ m})$ (eV)	0	-13.59844	0	0
$E_{100}(100\text{ m})$ (eV)	5.63881	3.90454	3.12220	4.92005

Table 15.319. The total bond energies of isoquinoline calculated using the functional group composition and the energies of Table 15.318 compared to the experimental values [21].

Formula	Name	$C^{\circ}C$	$C^{\circ}H$	$C-C$	$C=N$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₉ H ₇ N	isoquinoline	8	7	1	3	85.48453	85.48338	0.00046

Table 15.320. The bond angle parameters of isoquinoline and experimental values [1]. E_p is $E_p(atom - atom, msr, AO)$.

Names of Angle	$2\alpha_1'$ Initial (α_1)	$2\alpha_2'$ Terminal (α_2)	$E_{p,calc}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{p,calc}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_1	c_2	c_3	c_4	E_p (eV)	θ_1 ($^\circ$)	θ_2 ($^\circ$)	θ_3 ($^\circ$)	Cal. θ ($^\circ$)	Exp. θ ($^\circ$)
$\angle C'CC$	2.63936	2.65034	-17.17218	20	-17.17218	20	1	0.79232	1	1	-1.83836	119.40			119.40	119.4 (naphthalene)
$\angle C'CH$												119.40			120.30	
$\angle C'NC_1$	2.54147	2.54147	-17.43216	22	-17.43216	24	1	0.78001	1	1	-1.83836				119.10	

INDOLE

Indole having the formula C_8H_7N comprises a phenyl moiety with a conjugated five-membered ring which comprises pyrrole except that one of the double bonds is part of the aromatic ring. The structure is shown in Figure. 74. The aromatic $C^{\text{3e}}=C$ and $C-H$ functional groups of the phenyl moiety are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section. The CH , NH , and $C_d = C_e$ groups of the pyrrole-type ring are equivalent to the corresponding groups of pyrrole, furan, and thiophene where present as given in the corresponding sections. The $C_b - C_d$ single bond of aryl carbon to the $C_d = C_e$ bond is also a functional group. This group is equivalent to the $C-C(O)$ group of benzoic acids with regard to $\Delta E_{H,MO}(AO/HO)$ in Eq. (15.42) and $E_T(\text{atom-atom}, msp^3.AO)$ in Eq. (15.52) both being -1.29147 eV . This energy is a linear combination of $\frac{-1.13379 \text{ eV}}{2}$, $E_T(\text{atom-atom}, msp^3.AO)$ of the $C-H$ group that the $C_b - C_d$ and $C-C(O)$ groups replace, and that of an independent $C2sp^3$ HO, -0.72457 eV (Eq. (14.151)). However, as in the case of pyrrole, the indole hybridization term c_2 is the aromatic $c_2(\text{benzene}C2sp^3HO) = 0.85252$ to match the aryl $C2sp^3$ HO, and the energy terms corresponding to oscillation in the transition state correspond to indole.

As in the case of pyrrole, the $C-N-C$ -bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1 = 2$ in Eqs. (15.42) and (15.52). The hybridization factor $c_2(\text{aryl}C2sp^3HO \text{ to } N) = 0.84665$ (Eq. (15.152)) matches the aromatic character of the $C2sp^3$ HOs to the N atom of the NH group, and C_2 and C_{2v} in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143), $C_2(\text{benzene}C2sp^3HO) = 0.85252$. Furthermore, $\Delta E_{H,MO}(AO/HO)$ in Eq. (15.42) and $E_T(\text{atom-atom}, msp^3.AO)$ in Eq. (15.52) are both -2.42526 eV which is a linear combination of $\frac{-1.13379 \text{ eV}}{2}$, $E_T(\text{atom-atom}, msp^3.AO)$ of the $C-H$ group that the $C_e - N$ bond replaces, and -1.85836 eV (Eq. (14.513)) which is equivalent to the corresponding component of the $C-N-C$ -bond of pyrrole.

The symbols of the functional groups of indole are given in Table 15.321. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of indole are given in Tables 15.322, 15.323, and 15.324, respectively. The total energy of indole given in Table 15.325 was calculated as the sum over the integer multiple of each $E_D(\text{group})$ of Table 15.324 corresponding to functional-group composition of the molecule. The bond angle parameters of indole determined using Eqs. (15.79-15.108) are given in Table 15.326.

Table 15.321. The symbols of functional groups of indole.

Functional Group	Group Symbol
CC (aromatic bond)	$C^{\text{3e}}=C$
CH (aromatic)	CH (i)
$C_d = C_e$ double bond	$C = C$
$C_h - C_d$	$C - C$
CH	CH (ii)
$C_e - N - C_e$	$C - N - C$
NH group	NH

Table 15.324. The energy parameters (eV) of functional groups of indole.

Parameters	C=C Group	CH (i) Group	C=C Group	CH (ii) Group	C-N-C Group	NH Group
f_1	0.75	1	1	1	1	1
n_1	2	1	2	1	2	1
n_2	0	0	0	0	0	0
n_3	0	0	0	0	0	0
C_1	0.5	0.75	0.5	0.75	0.5	0.75
C_2	0.85252	1	0.85252	1	0.85252	0.93613
C_3	1	1	1	1	1	0.75
C_4	0.85252	0.91771	0.85252	0.91771	0.84665	0.92171
C_5	0	1	0	1	0	1
C_6	3	1	4	1	4	1
C_7	0	1	0	1	0	1
C_{10}	0.5	0.75	0.5	0.75	0.5	0.75
C_{11}	0.85252	1	0.85252	1	0.85252	1
V_e (eV)	-101.12679	-37.10024	-32.93291	-39.09338	-104.73877	-39.48897
V_p (eV)	20.69825	13.17125	20.85777	13.45505	20.90891	14.45367
T (eV)	34.31559	11.58941	35.96751	12.74462	36.26840	15.88820
V_p (eV)	-17.15779	-5.79470	-17.98376	-4.53884	-18.13420	-7.93410
f_2 (a.u.)	0	-14.63489	0	-14.63489	0	-14.53414
$\Delta E_{H_{1st}}$ (eV)	0	-1.13719	-2.26759	-1.29147	-2.43256	0
E_{1st} (eV)	0	-13.50110	2.26759	-13.34342	2.42576	-14.53414
E_{2nd} (eV)	-63.27075	-31.63539	-63.27075	-31.63539	-63.27040	-31.63534
E_{3rd} (eV)	-2.26759	-0.56690	-2.26759	-1.29147	-2.43256	0
E_{4th} (eV)	-65.53833	-32.20226	-65.53833	-32.92684	-65.69600	-31.63537
ω [10^{15} rad/s]	49.7272	26.4826	15.4421	21.8249	54.5632	48.7771
E_c (eV)	32.73133	17.43132	10.16428	14.36554	35.91442	32.10594
E_p (eV)	-0.33806	-0.26130	-0.20668	-0.24690	-0.38945	-0.35462
E_{1st} (eV)	0.19649	0.35532	0.17897	0.12312	0.11159	0.40696
E_{2nd} (eV)	-0.25982	-0.08364	-0.11720	-0.18534	-0.07587	-0.15115
E_{3rd} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E_{4th} (eV)	-49.44347	-32.28590	-65.77272	-33.11218	-66.36330	-31.78651
E_{5th} (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414
E_{6th} (eV)	0	-13.59844	0	-13.59844	0	-13.59844
E_{7th} (eV)	5.63881	3.90454	7.23317	3.84240	7.82374	3.51208

Table 15.325. The total bond energies of indole calculated using the functional group composition and the energies of Table 15.374 compared to the experimental values [2].

Formula	Name	$\sum C=C$	CH (I)	C=C	C-C	CH (II)	C-N-C	NH	Total Bond Energy (eV)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₈ H ₇ N	Indole	6	4	1	1	2			78.5213	78.514		-0.0070

Table 15.326. The bond angle parameters of indole and experimental values [1]. In the calculation of θ_p , the parameters from the preceding angle were used. E_r is $E_r(\text{atom} - \text{atom}, \text{m.p.}, \text{AO})$.

Atom or Angle	$2c^*$ (rad)	$2c^*$ (deg)	$2c^*$ Terminal (deg)	E_{center} Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	E_{center} Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_1 Atom 1	c_1 Atom 2	C_1	C_2	C_3	C_4	C_5	C_6	θ_p (°)	θ_q (°)	θ_r (°)	θ_s (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_1C_2C_3$ (aromatic)	2.62936		4.5585	-17.17218	20	-17.17218	20	0.79332	0.79332	1	1	1	1	1	1					120.19	120 [50-52] (benzene)
$\angle C_2C_3C_4$ (aromatic)																				120.19	120 [50-52] (benzene)

ADENINE

Adenine having the formula $C_5H_5N_5$ comprises a pyrimidine moiety with an aniline group and a conjugated five-membered ring which comprises imidazole except that one of the double bonds is part of the aromatic ring. The structure is shown in Figure. 75. The aromatic $\overset{3e}{C}=C$, $C-H$, and $\overset{3e}{C}=N$ functional groups of the pyrimidine moiety are equivalent to those of pyrimidine as given in the corresponding section. The NH_2 and C_a-N_a functional groups of the aniline moiety are equivalent to those of aniline as given in the corresponding section. The CH , NH , C_d-N_e , and $N_e=C_e$ groups of the imidazole-type ring are equivalent to the corresponding groups of imidazole as given in the corresponding section. The $C-N-C$ functional group of the imidazole-type ring is equivalent to the corresponding group of indole having the same structure with the $C-N-C$ group bonding to aryl and alkenyl groups.

The symbols of the functional groups of adenine are given in Table 15.327. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of adenine are given in Tables 15.328, 15.329, and 15.330, respectively. The total energy of adenine given in Table 15.332 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.330 corresponding to functional-group composition of the molecule. The bond angle parameters of adenine determined using Eqs. (15.79-15.108) are given in Table 15.332.

Table 15.327. The symbols of functional groups of adenine.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{3e}{C}=C$
CH (aromatic)	CH (i)
$\overset{3e}{C}_{b,c}=N_c$ $\overset{3e}{C}_{a,b}=N_b$	$\overset{3e}{C}=N$
C_a-N_a	$C-N$ (a)
NH_2 group	NH_2
$N_e=C_e$ double bond	$N=C$
C_d-N_e	$C-N$ (b)
N_dH group	NH
CH	CH (ii)
$C_c-N_d-C_e$	$C-N-C$

Table 15.328. The geometrical bond parameters of adenine and experimental values [1].

Parameter	C-C Group	CH (i) Group	C-N Group	C-N (a) Group	NH ₂ Group	N=C Group	C-N (b) Group	NH Group	CH (i) Group	C-N-C Group
σ (Å)	1.3748	1.6061	1.47169	1.81158	1.24428	1.4926	1.82450	1.24428	1.53180	1.44594
σ' (Å)	1.31468	1.03299	1.27073	1.34595	0.94134	1.0383	1.35074	0.94134	1.01120	1.30144
Bond Length $2\sigma'$ (Å)	1.39140	1.09327	1.34489	1.42449	0.99627	1.37991	1.42956	0.996270	1.07021	1.37738
Exp. Bond Length $2\sigma'$ (Å)	1.393 (pyrimidine)	1.084 (pyrimidine)	1.340 (pyrimidine)	1.431 (aniline)	0.998 (aniline)			0.996 (pyrimidine)	1.076 (pyrimidine)	1.370 (pyrimidine)
$h\sigma$ (Å)	0.66540	1.22265	0.74237	1.21254	0.81370	0.63276	1.22650	0.81370	1.15326	0.63548
σ	0.89223	0.64537	0.86245	0.74297	0.76553	0.89955	0.74033	0.76553	0.63928	0.80131

Table 15.329. The MO to HO intercept geometrical bond parameters of adenine. R_i is an allyl group and R_i, R_j, R_k are H or allyl groups. E_i is E_i (atom - atom, σ_{sp}^2 , ΔO).

Bond	Atom	E_i (eV) Bond 1	E_j (eV) Bond 2	E_k (eV) Bond 3	E_l (eV) Bond 4	Final Total Energy C_{2sp}^2 (eV)	r_{atom} (Å)	r_{atom} (Å) Final	E_{atom} (eV) Final	E_{atom} (eV) Final	θ_i (°)	θ_j (°)	θ_k (°)	θ_l (°)	d_i (Å)	d_j (Å)	d_k (Å)	d_l (Å)
$C_2(N_1)C_2(N_2)H-H$	N_1	-0.56090	0	0	0	-0.56090	0.93044	0.88072	-15.37065	121.74	38.26	67.49			0.7004			0.46000
$C_2(N_1)C_2(N_2)H-H_1$	C_2	-0.56090	-0.54343	-0.83035	0	-153.27026	0.91771	0.81052	-16.70618	90.90	90.10	41.93			1.31727			0.00142
$C_2(N_1)C_2(N_2)H-H_2$	N_2	-0.56090	0	0	0	-153.27026	0.93044	0.88072	-15.37065	96.33	83.68	46.43			1.28459			0.00756
$C-H (C_2H)$	C_1	-0.54343	-0.54343	-0.56090	0	-153.26943	0.91771	0.82662	-16.47951	78.27	101.75	41.29			1.30084			0.16785
$C-H (C_2H)$	C_2	-0.56090	-0.54343	0	0	-153.27026	0.91771	0.81052	-16.70618	79.01	100.29	41.89			1.31529			0.15660
$N-H (N_1H)$	N_1	-0.60031	-0.60031	0	0	-153.27026	0.93044	0.88072	-16.00838	119.52	60.48	63.13			0.52338			0.41796
$C_2(N_1)C_2(N_2)H-H_1$	C_2	-0.56090	-0.54343	-0.56090	0	-153.27026	0.91771	0.81052	-16.70618	121.54	51.46	58.65			0.76572			0.30101
$C_2(N_1)C_2(N_2)H-H_2$	N_2	-0.56090	-0.54343	0	0	-153.27026	0.93044	0.88072	-15.31261	130.61	49.39	60.57			0.71418			0.55456
$N_1(N_1)C_2(N_2)H-H_1$	C_1	-0.54343	-0.54343	-0.56090	0	-153.26943	0.91771	0.82662	-16.47951	129.28	50.74	59.44			0.74824			0.32349
$N_1(N_1)C_2(N_2)H-H_2$	C_2	-0.56090	-0.54343	-0.60031	0	-153.27026	0.91771	0.81052	-16.70618	128.45	51.55	58.55			0.76792			0.30281
$N_1(N_1)C_2(N_2)H-H_3$	C_2	-0.56090	-0.54343	-0.56090	0	-153.27026	0.91771	0.81052	-16.70618	134.83	45.13	59.72			0.74304			0.37165
$C_2(N_1)C_2(N_2)H-H_4$	C_1	-0.56090	-0.54343	-0.44599	0	-153.27026	0.91771	0.88076	-16.09103	134.44	45.56	59.22			0.73528			0.16071
$C_2(N_1)C_2(N_2)H-H_5$	C_1	-0.56090	-0.54343	-0.60031	0	-153.27026	0.91771	0.81052	-16.70618	134.77	45.23	59.62			0.74016			0.16932
$C_2(N_1)C_2(N_2)H-H_6$	C_2	-0.56090	-0.54343	-0.60031	0	-153.27026	0.91771	0.81052	-16.70618	137.54	42.46	60.78			0.76488			0.19616
$N_1(N_1)C_2(N_2)H-H_7$	N_2	-0.60031	-0.60031	0	0	-153.27026	0.93044	0.88076	-16.09103	135.04	46.95	62.76			0.66883			0.16161
$N_1(N_1)C_2(N_2)H-H_8$	C_1	-0.60031	-0.59218	0	0	-153.26943	0.91771	0.81052	-16.70618	138.42	41.59	61.93			0.67540			0.16203
$C_2(N_1)C_2(N_2)H-H_9$	C_2	-0.56090	-0.54343	0	0	-153.27026	0.91771	0.81052	-16.70618	137.03	42.07	61.72			0.68657			0.16176
$C_2(N_1)C_2(N_2)H-H_{10}$	N_2	-0.56090	-0.54343	0	0	-153.27026	0.93044	0.88076	-16.09103	132.20	41.80	62.08			0.67849			0.16334
$C_2(N_1)C_2(N_2)H-H_{11}$	N_2	-0.56090	-0.54343	0	0	-153.27026	0.93044	0.88076	-16.09103	91.32	88.68	43.14			1.23153			0.01939
$C_2(N_1)C_2(N_2)H-H_{12}$	C_1	-0.56090	-0.54343	-0.83035	0	-153.27026	0.91771	0.88076	-16.09103	87.71	91.19	40.72			1.30380			0.03106

Table 15.330. The energy parameters (eV) of functional groups of adenine.

Parameters	C=C Group	CH (i) Group	C=N Group	C-N (a) Group	NH ₂ Group	N=C Group	C-N (b) Group	NH Group	CH (ii) Group	C-N-C Group
f_1	0.75	1	0.75	1	1	1	1	1	1	1
f_2	2	1	2	1	2	2	1	1	1	2
f_3	0	0	0	0	0	0	0	0	0	0
f_4	0	0	0	0	1	0	0	0	0	0
C_1	0.5	0.75	0.5	0.5	0.75	0.5	0.5	0.75	0.75	0.5
C_2	0.85252	1	0.91140	1	0.95613	0.85252	1	0.95613	1	0.85252
C_3	1	1	1	1	0.75	1	1	0.75	1	1
C_4	0.85252	0.91771	0.91140	0.84665	0.92171	0.84665	0.84665	0.92171	0.91771	0.84665
C_5	0	1	0	0	0	0	0	1	1	0
C_6	3	1	3	2	1	4	2	1	1	4
C_7	0	1	0	0	2	0	0	1	1	0
C_8	0.5	0.75	0.5	0.5	1.5	0.5	0.5	0.75	0.75	0.5
C_{9a}	0.85252	1	0.91140	1	1	0.85252	1	1	1	0.85252
V_1 (eV)	-101.12679	-37.10024	-102.01431	-32.70465	-78.97795	-103.97756	-32.44864	-39.48897	-39.09538	-104.73877
V_2 (eV)	20.69825	13.17125	21.41410	10.10870	28.90735	20.87050	10.07785	14.43367	13.45505	20.90891
T (eV)	34.31559	11.58941	34.65890	9.04312	31.73641	35.85539	8.89248	15.86820	12.74462	36.26840
V_3 (eV)	-17.15779	-5.79470	-17.32945	-4.52156	-15.86820	-17.92770	-4.46524	-7.93410	-6.37231	-18.13420
$E_{1,100}$ (eV)	0	-14.63489	0	-14.63489	-14.53414	0	-14.63489	-14.53414	-14.63489	0
$\Delta E_{1,100}$ (eV)	0	-1.13379	0	-1.13379	0	-1.85836	-0.92918	0	-2.6758	-2.02526
$E_{2,100}$ (eV)	0	-13.50110	0	-13.50110	-14.53414	1.85836	-13.70571	-14.53414	-12.36751	2.42526
$E_{3,100}$ (eV)	0	0	0	0	-14.53414	0	0	0	0	0
$E_{4,100}$ (eV)	-63.27075	-31.63339	-63.27076	-31.63369	-48.73654	-63.27100	-31.63327	-31.63534	-31.63553	-63.27040
$E_{5,100}$ (eV)	-2.36759	-0.56690	-1.44915	-1.13379	0	-1.85836	-0.92918	0	0	-2.42526
$E_{6,100}$ (eV)	-65.53833	-32.20226	-64.71988	-32.76916	-48.73660	-65.13910	-32.36455	-31.63537	-31.63537	-65.69600
ω (10 ⁴ mol/s)	49.7272	26.4826	43.6311	11.9890	68.9812	15.4704	21.5213	48.7771	28.9084	54.5632
E_7 (eV)	32.71133	17.43132	28.71875	7.89138	45.40465	10.18290	14.16571	32.10394	19.02803	35.91442
E_8 (eV)	-0.35806	-0.26130	-0.33540	-0.18211	-0.42172	-0.20558	-0.24248	-0.35462	-0.27301	-0.38945
$E_{1,100}$ (eV)	0.19649	0.35352	0.19649	0.15498	0.00239	0.20768	0.12944	0.40636	0.39427	0.11159
$E_{2,100}$ (eV)	[49]	E_8 (15.458)	[49]	[54]	[23]	[58]	[23]	[24]	[56]	[12]
$E_{3,100}$ (eV)	-0.23982	-0.08364	-0.23715	-0.10462	-0.21708	-0.10174	-0.17775	-0.15115	-0.07587	-0.33565
$E_{4,100}$ (eV)	0.14803	0.14803	0.09457	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{5,100}$ (eV)	-40.54347	-32.28590	-48.82472	-32.87379	-49.17075	-65.33259	-32.74230	-31.78651	-31.71124	-66.36330
$E_{6,100}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489
$E_{7,100}$ (eV)	0	-13.59844	0	0	-13.59844	0	0	-13.59844	-13.59844	0
$E_{8,100}$ (eV)	5.63881	3.50454	4.92005	3.60401	7.43973	6.79503	3.47753	3.51208	3.52988	7.82374

Table 15.331. The total bond energies of adenine calculated using the functional group composition and the energies of Table 15.330 compared to the experimental values [2].

Formula	Name	C=C	CH (i)	C=N	C-N (a)	NH ₂ Group	N=C	C-N (b)	NH	CH (ii)	C-N-C	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₄ H ₄ N ₄	Adenine	2	1	4	1	1	1	1	1	1	1	70.5753	70.7981	-0.00035

Table 15.332. The bond angle parameters of adenine and experimental values [61]. In the calculation of θ_i , the parameters from the preceding angle were used. ε_i is $F_{T, \text{atom}} - \text{atom, mp } AO$.

Atom of Angle	$2\phi_1$ True 1 (ϕ_1)	$2\phi_2$ True 2 (ϕ_2)	$2\phi_3$ True 3 (ϕ_3)	Γ_{amide} Atom 1 (ϕ_1)	Atom 1 Hybridization Designation (Table 15.3B)	F_{amide} Atom 3	Atom 3 Hybridization Designation (Table 15.3B)	ε_1 Atom 1	ε_2 Atom 2	C_1	C_2	ε_i	ε_j	θ_i ($^\circ$)	θ_j ($^\circ$)	Col. θ ($^\circ$)	Exp. θ ($^\circ$)
$\angle HNH$	1.8264	1.8264	3.1559	-14.53414	N	H	H	0.95613 (15.120)	0.8234 (15.120)	1	1	0.75	1.0423			113.89	113.7 (1) (allied)
$\angle HNC''$	1.8264	2.6190	4.0497	-14.53414	N	-15.95955	6	0.8465 (15.152)	0.8234 (15.152)	0.75	1	0.75	1.01912			123.60	118
$\angle HC''N''$	2.60598	2.54147	3.9497	-14.82575	1	-14.53414	N	0.91771 (15.116)	0.9140 (15.116)	0.75	1	0.75	0.99312			117.65	115 116
$\angle HC''N''$	2.02241	2.60746	4.0661	-16.36125	10	-14.53414	N	0.83159 (15.132)	0.8465 (15.132)	0.75	1	0.75	1.01811			122.35	126
$\angle HC''N''$														122.35	112.64	124.02	119
$\angle HN''N''$	1.8264	2.60287	4.0497	-14.53414	N	-15.95955	6	0.8465 (15.152)	0.8234 (15.152)	0.75	1	0.75	1.00912			128.35	127
$\angle NC''N''$	2.60746	2.60287	4.3559	-16.21952	8	-16.03938	7	0.91140 (15.132)	0.8465 (15.132)	1	1	1	0.84359			112.64	114.4
$\angle NC''N''$	2.54147	2.60287	4.6260	-14.53414	N	-14.53414	N	0.8465 (15.152)	0.8465 (15.152)	1	1	1	0.87902			128.11	127.8
$\angle NC''N''$	2.54147	2.54147	4.5826	-15.55033	3	-15.55033	3	0.87495 (15.116)	0.87495 (15.116)	1	1	1	0.87495			128.73	128.9
$\angle NC''N''$	2.54147	2.60190	4.5826	-15.91261	5	-15.39266	2	0.85503 (15.132)	0.83982 (15.132)	1	1	1	0.86947			122.22	119.7
$\angle NC''C''$	2.70148	2.60936	4.3818	-14.53414	N	-15.95955	6	0.8465 (15.152)	0.83522 (15.152)	1	1	1	0.84958			110.56	110.4
$\angle NF''C''$	2.60287	2.60936	4.1932	-14.53414	N	-16.99103	16	0.8465 (15.152)	0.80076 (15.152)	1	1	1	0.82371			106.60	105.9
$\angle NC''C''$	2.54147	2.60936	4.4721	-14.53414	N	-16.99103	16	0.8465 (15.152)	0.80076 (15.152)	1	1	1	0.83508			119.73	126.4
$\angle NC''C''$	2.54147	2.60936	4.4721	-14.53414	N	-16.99103	16	0.8465 (15.152)	0.80076 (15.152)	1	1	1	0.85608			119.73	118.2
$\angle NC''C''$	2.60190	2.60936	4.5607	-14.53414	N	-16.52644	12	0.8465 (15.152)	0.82327 (15.152)	1	1	1	0.86734			117.97	122.1
$\angle NC''C''$	2.70148	2.60936	4.8990	-14.53414	N	-14.82575	1	0.8465 (15.152)	0.91771 (15.152)	1	1	1	0.91556			135.55	132.8
$\angle C''N''C''$	2.70148	2.60936	4.2661	-17.92022	28	-17.92022	28	0.91924 (15.116)	0.91924 (15.116)	1	1	1	0.75924			106.93	103.3
$\angle C''N''C''$	2.60287	2.60347	4.2661	-17.75302	25	-17.75302	25	0.76631 (15.116)	0.76631 (15.116)	1	1	1	0.76631			110.07	106.1
$\angle C''N''C''$	2.54147	2.54147	4.3389	-17.90869	21	-17.75302	25	0.78155 (15.116)	0.78155 (15.116)	1	1	1	0.77959			118.09	111.3
$\angle C''N''C''$	2.54147	2.54147	4.3704	-17.71560	24	-17.40869	21	0.76801 (15.116)	0.78135 (15.116)	1	1	1	0.77478			119.59	118.6
$\angle C''C''C''$	2.60936	2.60936	4.4721	-17.71560	24	-17.40869	21	0.76801 (15.116)	0.78135 (15.116)	1	1	1	0.78071			116.52	116.7

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While the claimed invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.